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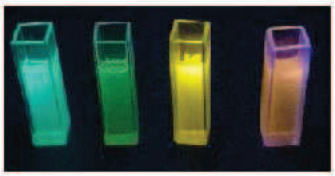
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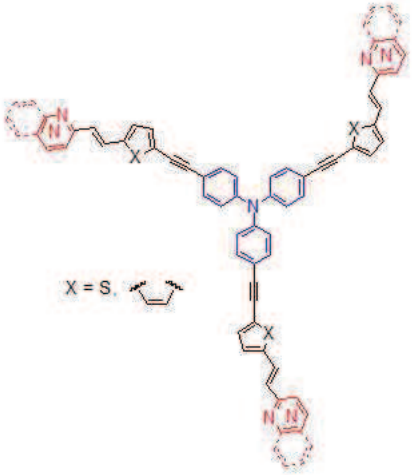
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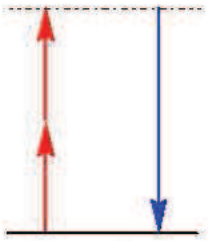
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Intense fluorescence
High emission solvatochromism





Two-photon absorption
δmax = 158-427 GM

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Tripodal molecules with triphenylamine core, diazine peripheral groups and extended π-conjugated linkers

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Abstract

A series of five octupolar molecules with central triphenylamine donor and peripheral diazine electron-withdrawing groups has been prepared. These structures possess extended π-spacer comprising multiple bonds in a combination with 1,4-phenylene and 2,5-thienylene subunits. Starting from tris(4-ethynylphenyl)amine, the key step in the preparation of the chromophores involves triple Sonogashira cross-coupling reaction. The photophysical properties of the compounds are described. A strong positive emission solvatochromism, typical for dyes featuring Intramolecular Charge Transfer (ICT), is observed, two-photon absorption (2PA) properties were also measured. Linear and nonlinear optical properties as well as electronic

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properties measured by cyclic voltametry and supported by DFT calculation were used to elucidate structure-property relationships.

Keywords: Diazines; Triphenylamines; Nonlinear Optics; Fluorescence; Intramolecular charge transfer

Introduction

During the past decade, organic molecules with a delocalized π-system of electron have been subject to numerous studies due to their prospective applications in field-effect transistor (OFETs),[1] organic light-emitting diodes (OLEDs)[2] and photovoltaic devices.[3] Among these systems, donor acceptor π-conjugated (D-π-A) materials, also called push-pull, represent a subclass with particular applications such as quadratic and cubic nonlinear optical (NLO) properties.[4] Intrinsic NLO properties of organic push-pull molecules are mainly dictated by the extent of ICT, which is originated by the D-A interaction and can easily be illustrated by two limiting resonance forms (aromatic and quinoid/zwitterionic arrangements).[5] In contrast to ordinary linear D-π-A molecules, star-shaped molecules with $D(-\pi-A)_3$ or $A(-\pi-D)_3$ arrangements exhibit enhanced ICT and further peculiar properties due to their unique structures and manifold transitions.[6] Branching of a push-pull molecule helps to reduce aggregation and to maintain luminescence in the solid state. Star-shaped structures are also known to bring cooperative enhancement in terms of conjugation expansion and two-photon absorption (2PA) properties.[7] Among others, triphenylamine represent undoubtedly the most frequent precursor used for the construction of $D(-\pi-A)_3$ molecules and its derivatives have been widely applied as 2PA-active substances. Triphenylamine core is considered as a moderate electron donor with propeller-shaped arrangement and C_3 symmetry and, therefore, displays an octupolar feature. Acceptor terminated triphenylamine derivatives were described as excellent 2PA chromophores.[8] Such chromophores have found applications

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for 2PA fluorescent microscopy,[9] cellular bioimaging,[10] 2PA-photodynamic therapy,[11] 3D optical data storage,[12] microfabrication,[13] three-photon absorbers,[14] organic solar cells,[15] molecular glasses,[16] guest molecules for intercalation and metal-organic frameworks (MOF)[17] as well as various detectors and sensors.[18]

Pyrimidine, pyrazine and quinoxaline (benzopyrazine) rings belong to the diazine heterocycles, which have been widely used as electron-withdrawing moieties in charge-transfer chromophores.[19] In particular, the 4,6-di(arylvinyl)pyrimidine motif has been synthetically well-established and push-pull molecules based on this scaffold delivered large 2PA cross-section.[20] Linear charge-transfer chromophores bearing diazine ring were investigated for their fluorescence,[21] 2nd order NLO[22] and 2PA properties.[23] Recently, Martin and coworkers have reported some star-shaped molecules with triphenylamine core and pyrimidine and pyridazine rings as peripheral groups and some of these tripodal molecules exhibited promising 2PA cross-section.[24] In general, the electron donor and acceptor as well as the π-conjugated bridge are integral parts of the D-π-A system and their optimization represents a key parameter to enhance the ICT and maximize the fluorescence intensity and 2PA cross-section.[5] Hence, the main purpose of the present article is to design and synthesize new star-shaped molecules **1-5** based on triphenylamine equipped with diazine peripheral acceptors and extended π-conjugated linkers (Chart 1). Influence of the length, planarity and composition of the π-linker as well as the nature of the diazine rings (nitrogen atom topology and further extension) on the photophysical and electronic properties will be thoroughly studied.

<Insert Chart 1.>

Results and discussion

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Preparation of star-shaped molecules. Arylvinyldiazines can easily be obtained by Knoevenagel condensation of corresponding aldehyde with commercially available methyldiazines. Vanden Eynde and co-workers described the synthesis of arylvinyldiazines using boiling aqueous 5 M NaOH in the presence of Aliquat 336 as a phase-transfer catalyst.[25] These conditions proved to be very efficient in the case of 4-methylpyrimidine and 2-methylquinoxaline and smoothly afforded bromo-substituted intermediates **6-9** in the yields of 54-79 % (Scheme 1). On the contrary, using 2-methylpyrazine and similar reaction condition provided only traces of the desired arylvinyldiazine **10**. This is most likely due to a lower acidity of the hydrogens appended at the methyl group. However, potassium hydroxide in DMSO (dimsyl potassium) at room temperature proved to be a sufficient base to abstract 2-methylpyrazine hydrogens[26] and subsequent reaction with 5-bromothiophene-2-carbaldehyde afforded compound **10** (Scheme 2). In this way, compound **10** was obtained in good yield and its purification was facile. Stereochemical outcome of the aforementioned Knoevenagel reactions was verified by ^{1}H NMR spectroscopy where all intermediates **6-10** showed pair of doublets with the coupling constants ^{3}J(H,H) about 16 Hz, which clearly evidences selective formation of (*E*)-configured compounds **6-10**.[27]

<Insert Scheme 1>

<Insert Scheme 2>

Arylvinyldiazines **6-10** were further used as coupling partners for the construction of target molecules **1-5** (Scheme 3). Threefold Sonogashira cross-coupling reaction with tris(4-ethynylphenyl)amine (**11**)[8a] carried out with Pd(0)-precatalysts, di*iso*propylamine, 1,4-dioxane and the temperature elevated up to 92 °C afforded star-shaped chromophores **1-5**. Besides tripodal molecules **1-5**, a formation of twofold and single cross-coupled products was

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also observed and could partially be suppressed by an excess of bromo derivatives **6-10**. However, the relatively low isolated yields of 23-60 % are mainly caused by difficult separation of **1-5** from the side products by column chromatography (repeated purifications were required). All of the new materials exhibited good solubility in a variety of solvents, especially in THF and chlorinated solvents. The ^{1}H, ^{13}C NMR and HRMS data were consistent with the expected structures.

<Insert Scheme 3>

UV-vis and Fluorescence Spectroscopy. The UV-Vis and photoluminescence (PL) spectroscopic data of star-shaped molecules **1-5**, measured in dichloromethane and in toluene at 25 °C, are presented in Tables 1 and S8. The analyses were carried out using low concentrated solutions (1.0 to 2.0 × 10^{-5} M for UV/Vis spectra and 1.0 to 3.0 × 10^{-6} M for PL spectra). As an example, the spectra for derivatives **1** and **4** in dichloromethane are shown in Figure 1. Under these conditions, self-absorption effects were not observed. All compounds proved to be photostable and none *E to Z* isomerization was observed under the given conditions.

<Insert Table 1>

<Insert Figure 1>

In dichloromethane, all target compounds exhibited absorption in visible region with the position of the longest-wavelength absorption maxima (λ_{max}) appearing at 401 to 436 nm. In all cases a second particularly developed band of higher energy was also observed. Molecular extinction coefficients of **1-5** (ε = 74.5 to 108.3 $mM^{-1}.cm^{-1}$) are approximately two to three times higher than that of corresponding linear molecules.[22a] Depending on the compound used, the emission maxima were observed in the green to orange region (λ_{max} = 555–630 nm). Interestingly, fluorescence

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quantum yields are relatively high (Φ_F = 0.37-0.67) even though the emission is red-shifted. Nevertheless, except for compound **2**, the fluorescence quantum yields are higher in toluene than in dichloromethane: a quantum yield up to 1.00 was observed for compound **1** in toluene. As expected for donor-acceptor functionalized π-conjugated molecules featuring the ICT, large Stokes shifts (up to 8340 cm^{-1}) were observed, which indicates large differences (vibrational, electronic, geometric) between the Franck-Condon state and the emissive excited state.

When comparing the nature of the peripheral diazine ring, the most red-shifted emissions were observed for quinoxaline compounds **3** and **4**, whereas the most hypsochromically shifted emission was observed for pyrazine substituted compound **5**. A similar trend was observed previously.[22e] The highest fluorescence quantum yield in dichloromethane is observed for pyrazine derivative **5**.

In general, replacement of 1,4-phenylene moieties in compounds **1** and **3** by 2,5-thienylene rings (compounds **2** and **4**) led to a red shift of both absorption and emission spectra. This is in accordance with the previous observation on linear push-pull chromophores.[28,5] However, in case of quinoxaline derivatives **3** and **4**, in dichloromethane, a blue-shifted emission is observed for thienylene derivative **4**.

In an effort to gain further insights into the photophysical process within these push-pull molecules, the absorption and emission behavior of the compounds **1-5** was studied in a variety of different aprotic solvents. While the positions of the longest-wavelength absorption maxima were not significantly affected, an increase in the solvent polarity led to bathochromic shifts of the emission maxima (Table 2). This behavior is generally observed for chromophores with ICT.[7d,9b,9d,21,22a] As an example, the spectra recorded for compound **2** are shown in Figure 2. When going from the least polar hexane (λ_{em} = 468 nm) to toluene, dioxane, THF, CH_2Cl_2 and acetone, the emission maxima was considerably red-shifted up to 618 nm ($\Delta\lambda_{em}$ = 150 nm resp. $\Delta\nu_{em}$ 5186 cm^{-1}). In more polar solvent such as MeCN or

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DMSO, the emission intensity was low and less detectable. When increasing the polarity, the emission spectra are less structured and emission bands are larger. To further illustrate strong emission solvatochromism of target star-shaped chromophores, Figure 3 shows the emission color of **4** in different solvents. Such behavior is consistent with a stabilization of the highly polar emitting excited states by polar solvents and has also been observed either for triphenylamine derivatives bearing electron-withdrawing groups[8b,9,29] or for diazines substituted with electron-donating substituents.[21,22a,22e,30] The emission solvatochromism represents one of the possible ways to evaluate ICT upon excitation in fluorescent molecules. Hence, the emission maxima were plotted *versus* the $E_T(30)$ Dimroth–Reichardt polarity parameters[31] (see the Supporting Information). For compounds **1-3** are the slope of the regression line slightly higher than for their linear analogues indicating a branching effect that enhances the ICT.[22a] When comparing the different diazine rings, quinoxaline derivatives **3** and **4** exhibited the highest regression line slopes. A replacement of 1,4-phenylene by 2,5-thienylene units in compounds **2** and **4** *versus* **1** and **3** tends to reduce the regression line slope and, therefore, chromophore **3** showed the highest regression line slope. When compared with star-shaped triphenylamine derivatives equipped with trifluoromethanesulfonate acceptors and similar π-conjugated linkers, the quinoxaline derivatives **3** and **4** showed very similar solvatochromic behavior.[32]

<Insert Table 2 >

<Insert Figure 2 >

<Insert Figure 3 >

Dichloromethane solutions of compounds **1-5** underwent an important color change upon addition of trifluoroacetic acid (TFA) with an important bathochromic shift of the absorption spectra (Figures 4-5). We had already observed this phenomenon, which is due to the protonation of the diazine ring that enhances its electron-withdrawing character and

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reinforce the ICT into the molecule.[21a,c,d,22c,e,33] These molecules appear therefore as potential colorimetric pH sensors. However, it should be noted that these color changes appear at higher concentration of TFA (10^{-2}-10^{-1} M) than for other diazine derivatives with shorter π-conjugated linker (10^{-5}-10^{-3} M).[34] On the other hand, the emission was totally quenched after treatment with acid, as is generally observed for amino electron donor substituted diazines.[21a,d,34]

<Insert Figure 4 >

<Insert Figure 5 >

Two photon absorption measurements. 2PA data of chromophores **1-5**, measured by relative two-photon excited fluorescence (2PEF) method, are presented in **Table 3**, and the 2PA spectra are shown in **Figure 6**. According to our spectral resolution, all octupoles exhibit a broad 2PA band whose maximum absorption wavelength is slightly lower than twice λ_{max} of the one photon absorption (1PA) band (see supporting information). The 2PA cross section (δ_{max}) are comprised between 158 and 427 GM. It is noteworthy that the thiophene-based derivatives **2** and **4** present another distinctive 2PA band around 940 nm. According to the Frenkel exciton model,[34] all those spectral effects should be ascribed to a significant interbranch coupling within these multipolar chromophores which leads to a splitting of the initially degenerate single excited levels associated to each molecular synthon.[7d,13a,35] Such a coupling is consequently responsible for the presence of multiple electronic π-π* transitions within the longest wavelength of the 1PA band as previously observed for similar trigonal branched structures.[7d,13a,35a,36,36] It should be noted that the 2PA cross sections are clearly enhanced on going from 1,4-phenylene group used as 'electron relay' to a 1,2-thienylene one (compounds **1** and **3** *versus* **2** and **4**). As expected, changing the pyrimidine end groups by pyrazine ones induces a noticeable decrease of δ_{max} (chromophores **1** *versus* **5**). However,

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interestingly, quinoxaline (benzopyrazine) derivatives **3** and **4** gave similar δ_{max} values in comparison with their pyrimidine analogues **1** and **2**. In term of action cross section, defined by the product of 2PA cross section and fluorescence quantum yield, compound **2** showed the highest figure of merit with $\Phi \times \delta_{max}$ = 248 GM.

<Insert Figure 6 >

<Insert Table 3 >

Electrochemical properties

Electrochemical behavior of chromophores **1-5** was investigated by cyclic voltammetry in DMF-$[Bu_4N][PF_6]$ at a scan rate of 0.1 V/s. The working electrode was a glassy carbon disk, tungsten wire was used as the counter electrode and a non aqueous Ag/Ag^+ electrode was used as reference. A representative CV diagram of chromophore **5** is shown in the SI, and the voltammogram shows two oxidation and two reduction waves. The second oxidation and the second reduction are irreversible processes. The first oxidation/reduction potentials as well as the electrochemical gap Eg^{elchem} and recalculated energies of the HOMO and the LUMO are presented in Table 4.

The first oxidation seems to be quasi-reversible, mostly one-electron process (irreversible for **4**) and most probably involve the central triphenylamine donor. The first reduction is a reversible two-electron process that may involve mostly diazine acceptor moiety and the adjacent π-system. The first oxidation/reduction potentials were found within the range of 0.61 to 0.69 and -2.02 to -1.70 V, respectively. Whereas the first oxidation is affected by the structural changes in **1** and **3-5** only negligibly, replacement of the peripheral diazine acceptor moieties and composition of the π-linker have significantly influenced the first reduction potentials in **1-5** and the corresponding electrochemical gap. A comparison of electrochemical behavior of chromophores **1**, **3** and **5** allows evaluation of pyrimidine, quinoxaline and pyrazine moieties. The quinoxaline strongest withdrawing property is

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reflected by the most positive reduction potential and the lowest electrochemical gap being measured for **3**. Replacement of 1,4-phenylene by 2,5-thienylene units in **1**/**2** and **3**/**4** shifted the first reduction positively, while the gaps of **3** and **4** are almost identical. Thus, chromophores **3**/**4** bearing the quinoxaline acceptor showed the lowest electrochemical gap as well as the most bathochromically shifted CT-bands, especially for **4** with 2,5-thienylene units. The same tendencies are observed for optical gap.

<Insert Table 4 >

Computational studies

The spatial and electronic properties of chromophores **1**-**5** were investigated using Gaussian W09 package[37] at the DFT level. The initial geometries of molecules **1**-**5** were estimated by PM3 method implemented in ArgusLab[38] and these were subsequently optimized by DFT HCTH/6-311+G(d) method. The energies of the HOMO and LUMO, their differences and ground state dipole moments were calculated with the DFT B3LYP/6-311++G(2d,p) and are summarized in Table 4.

The calculated energies of the HOMO and LUMO of **1**-**5** were found within the same range as electrochemically measured values as can be seen on the energy level diagram shown in Figure 7. Moreover, both energies correlate tightly and, therefore, the used DFT method can be considered as a reasonable tool for description of the electronic properties of **1**-**5** (see the SI).

<Insert Figure 7>

Very similar trends as seen by the CV measurements can also be deduced from the DFT calculated energies of the HOMO and LUMO and their differences. The HOMO-LUMO gap can be reduced by replacement of the peripheral acceptor within the order of **5** > **1** > **2** > **3**

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> **4**. Chromophores **3** and **4** bearing the most electron withdrawing quinoxaline moieties possess the lowest calculated gaps of 2.54 and 2.31 eV. The latter is further reduced by the presence of 2,5-thienylene instead of 1,4-phenylene π-linker. Positions of the frontier molecular orbitals in **1**-**5** are visualized in Figure 8. The HOMO is localized on the central amino donor and adjacent alternating positions of the triphenylamine core, whereas the LUMO is spread over the peripheral diazine acceptors and the adjacent π-linker. Both frontier orbitals are clearly separated which further confirms CT character of chromophores **1**-**5**.

<Insert Figure 8 >

Considering tripodal character and C3 symmetry group of each derivative **1**-**5**, the LUMO is localized over one or two particular branche(s). The third branch is occupied by the LUMO+1. The HOMO as well as the HOMO-1 remained on the central amino donor. This is a common feature and has already been observed earlier for tripodal molecules based on triphenylamine.[8a,39] As expected, the calculated ground state dipole moments μ_G are modest within the range of 0.08 to 4.79 D, which reflects tripodal character of chromophores **1**-**5**.

Conclusions

In summary, we have successfully synthesized and characterized a series of triphenylamine-based tripodal molecules bearing peripheral diazine electron-attracting groups. The key step of their synthesis involves threefold Sonogashira cross-coupling reaction between tris(4-ethynylphenyl)amine (donor central part) and the corresponding bromoarylvinyldiazine derivatives (peripheral acceptors). These compounds exhibit absorption in the blue region and are highly luminescent with significant Stokes shifts. For all the compounds a strong emission solvatochromism was observed in a variety of non-polar solvents. This finding supports formation of a very polar excited ICT state. These materials exhibit 2PA properties, measured by 2PA excited fluorescence spectroscopy within the spectral range of 700 to 1020 nm. 2PA cross sections up to 427 GM were obtained. The HOMO and LUMO levels were estimated by

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cyclic voltametry measurements and DFT calculations. From all the performed measurements and calculations is apparent that derivatives **2** and **4**, bearing 2,5-thienylene spacer, exhibit the highest 2PA cross section and the lowest HOMO-LUMO gap even if their solvatochromic ranges are lower than that of their 1,4-phenylene analogues. The pyrimidine and quinoxaline derivatives display similar 2PA cross sections but quinoxaline compounds showed lower HOMO-LUMO gap. In view of the current wide and general interest in novel 2PA absorbers, we believe that this joint study would be considered as a very useful guide in designing octopolar tripodal molecules bearing diazine peripheral acceptor groups.

Experimental Section

General. Compounds **6-8** were obtained according to reported procedures.[22a,22e] Compound **11** was obtained from tris(4-iodophenyl)amine and TMSA by Sonogashira cross-coupling reaction according to reported procedure.[8a,40] All air- and moisture-sensitive reactions were carried out in flame-dried glassware subsequently cooled under nitrogen. NMR spectra were acquired at room temperature on a Bruker AC-300 spectrometer. Chemical shifts are given in parts per million relative to TMS (^{1}H, 0.0 ppm) and $CDCl_3$ (^{13}C, 77.0 ppm). Acidic impurities in $CDCl_3$ were removed by treatment with anhydrous K_2CO_3. High resolution mass analyses were performed at the "Centre Régional de Mesures Physiques de l'Ouest" (CRMPO, University of Rennes1) using a Bruker MicroTOF-Q II apparatus. IR spectra were recorded on a Perkin–Elmer spectrum1000 FTIR using KBr plates. UV/vis spectra were recorded with a UVIKON xm SECOMAM spectrometer using standard 1 cm quartz cells. Fluorescence spectra were recorded using Spex FluoroMax-3 Jobin-Yvon Horiba apparatus. Compounds were excited at their absorption maxima (longest-wavelength absorption band) to record the emission spectra. The Φ_F values were calculated using a well-known procedure using 9,10-diphenylethynylanthracene in cyclohexane as standard.[41] Stokes shifts were calculated by considering the lowest energetic absorption band.

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2PA measurement. The two-photon absorption (2PA) measurements were performed with femtosecond mode-locked laser pulse using a Ti: Sapphire laser (Coherent, Chameleon Ultra II: pulse duration: ~140 fs; repetition rate: 80 MHz; wavelength range: 680-1040 nm). A relative 2PEF method[42] was employed to measure the two-photon absorption cross-sections, δ. The measurements of 2PA cross-sections were performed relative to reference molecules (*r*) such as fluorescein[40,43] in water at pH = 11. The value of δ for a sample (*s*) is given by:

$$\delta_S = \frac{S_S \Phi_r \eta_r c_r}{S_r \Phi_S \eta_S c_S} . \delta_r$$

Where *S* is the detected two-photon excited fluorescence integral area, *c* the concentration of the chromophores, and Φ is the fluorescence quantum yield of the chromophores. η is the collection efficiency of the experimental set-up and accounts for the wavelength dependence of the detectors and optics as well as the difference in refractive indices between the solvents in which the reference and sample compounds are dissolved. The measurements were conducted in a regime where the fluorescence signal showed a quadratic dependence on the intensity of the excitation beam, as expected for two-photon induced emission. For the calibration of the two-photon absorption spectra, the two-photon excited fluorescence signal of each compound was recorded at the same excitation wavelength as that used for standards (i.e. λ_{exc} = 782 nm for fluorescein). The laser intensity was in the range of 0.2-2 x 10^9 W/cm^2. The experimental error on the reported cross section is 15 %.

(*E*)-2-(2-(5-Bromothiophen-2-yl)vinyl)quinoxaline (9): 2-Methylquinoxaline (720 mg, 5.00 mmol) and 5-bromothiphene-2-carbaldehyde (955 mg, 5.00 mmol) were added to a solution of NaOH (25 mL, 5M) with addition of approx. 100 mg (0.25 mmol) of Aliquat® 336. The resulting emulsion was heated up to reflux for 2 h. After cooling to 25 °C, the gummy-like precipitate was decanted, washed with water (2 × 25 mL) and dried *in vacuo*. The crude

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product was crystallized from DCM/*n*-heptane to afford 860 mg (54 %) of **9** as a brownish yellow solid. Mp: 107-109 °C ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) : 7.02 – 7.07 (m, 3H), 7.73 (dquint, 2H, ^{3}J = 6.9 Hz, ^{4}J = 1.5 Hz), 7.89 (d, 1H, ^{3}J = 15.9 Hz), 8.04 (dt, 2H, ^{3}J = 6.9 Hz, ^{4}J = 1.5 Hz), 8.92 (s, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) :114.2 (C), 124.6 (CH), 128.3 (CH), 129.1 (CH), 129.2 (CH), 129.3 (2 × CH), 130.4 (CH), 131.0 (CH), 141.6 (C), 142.5 (C), 143.2 (C), 144.5 (CH), 149.9 (C). IR (ATR) ν: 3058, 1620, 1426, 1415, 947, 752 cm^{-1} HRMS (ESI/ASAP) m/z calculated for $C_{14}H_{10}{}^{79}BrN_2S$ $[M+H]^+$ 316.9748, found 316.9749.

(*E*)-2-(4-Bromostyryl)pyrazine (10): 4-Bromobenzaldehyde (2.30 g, 12.5 mmol) and 2-methylpyrazine (1.17 g, 12.5 mmol) were dissolved in DMSO (7.5 mL). Powdered KOH (2.75 g, 50.0 mmol) was added and the reaction mixture was stirred at room temperature for 8 h and then poured into 200 mL of water. The resulting precipitate was filtered and washed with water (2 × 150 mL). The crude product was crystallized from DCM/*n*-heptane to afford **10** (2.01 g, 62 %) as a brownish yellow solid. Mp: 110-112 °C ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) : 7.14 (d, 1H, ^{3}J = 16.2 Hz), 7.45 (d, 2H, ^{3}J = 8.7 Hz), 7.52 (d, 2H, ^{3}J = 3.4 Hz), 7.68 (d, 1H, ^{3}J = 16.2 Hz), 8.42 (d, 1H, ^{3}J = 2.4 Hz), 8.54 (dd, 1H, ^{3}J = 2.4 Hz, ^{4}J = 1.2 Hz), 8.62 (d, 1H, ^{4}J = 1.2 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) : 123.0 (C), 124.7 (CH), 128.7 (CH), 132.0 (CH), 133.9 (CH), 135.0 (C), 143.0 (CH), 143.8 (CH), 144.4 (CH), 150.9 (C). IR (ATR) ν: 3048, 1487, 1403, 1009, 964 cm^{-1} HR-MS MALDI (matrix DHB): m/z calculated for $C_{12}H_{10}{}^{79}BrN_2$ $[M+2H]^+$ 262.0095, found 262.0102.

General procedure for Sonogashira cross-coupling reaction: A mixture of 4,4‘,4‘‘-tris(ethynyl)triphenylamine **11** (80 mg, 0,25 mmol) and the corresponding bromo derivative (0.91 mmol) was dissolved in a mixture of 1,4-dioxane (20 mL) and di*iso*propylamine (5 mL). Nitrogen was bubbled through the mixture for 10 min whereupon $[Pd(PPh_3)_4]$ (29 mg, 0.025

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mmol, 10 %) and CuI (9 mg, 0.05 mmol, 20 %) were added and the reaction mixture was stirred 92 °C for 12 h. The reaction was quenched with water (50 mL), extracted with DCM (2 × 100 mL) and the combined organic extracts were dried over $MgSO_4$ and the solvents were evaporated *in vacuo*. The crude product was purified by column chromatography with the indicated stationary phase and the solvent system.

Tris-{4-[4-((*E*)-2-pyrimidin-4-yl-vinyl)-phenylethynyl]-phenyl}-amine (1): The title compound was obtained from **6** following the general procedure for Sonogashira cross-coupling reaction and was purified by column chromatography (Al_2O_3, EtOAc). Yellow solid (81 mg, 38 %. Mp: 190 °C (dec.). ^{1}H-NMR (300 MHz, CD_2Cl_2): δ (ppm) : 7.12 – 7.18 (m, 9H), 7.38 (dd, 3H, ^4J = 1.2 Hz, ^3J = 5.4 Hz), 7.52 (d, 6H, ^3J = 9.0 Hz), 7.59 (d, 6H, ^3J = 8.4 Hz), 7.67 (d, 6H, ^3J = 8.4 Hz), 7.94 (d, 3H, ^3J = 15.9 Hz), 8.71 (d, 3H, ^3J = 5.4 Hz), 9.16 (d, 3H, ^4J = 1.2 Hz). ^{13}C-NMR (75 MHz, CD_2Cl_2): δ (ppm) : 89.5 (C), 91.5 (C), 118.2 (C), 119.2 (CH), 124.5 (CH), 124.7 (C), 126.9 (CH), 128.0 (CH), 132.3 (CH), 133.2 (CH), 135.9 (C), 136.5 (CH), 147.3 (C), 157.9 (CH), 159.2 (CH), 162.3 (C). IR (ATR) ν: 2208 (C≡C), 1573, 1512, 1090, 833 cm^{-1} HRMS MALDI (matrix DHB) m/z calculated for $C_{60}H_{39}N_7$ [M^+] 857.3267, found 857.3270.

Tris-{4-[5-((*E*)-2-pyrimidin-4-yl-vinyl)-thiophen-2-ylethynyl]-phenyl}-amine (2): The title compound was obtained from **7** following the general procedure for Sonogashira cross-coupling reaction and was purified by column chromatography (Al_2O_3, EtOAc). Reddish-orange solid (61 mg, 28 %). Mp: 110 °C (dec). ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) : 6.83 (d, 3H, ^3J = 15.9, Hz), 7.11 (d, 6H, ^3J = 8.7 Hz), 7.19 (d, 3H, ^3J = 3.4 Hz), 7.20 (d, 3H, ^3J = 3.4 Hz), 7.27-7.26 (m, 3H), 7.46 (d, 6H, ^3J = 8.7 Hz), 8.01 (d, 3H, ^3J = 15.9, Hz), 8.68 (d, 3H, ^3J = 5.1 Hz), 9.16 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) : 82.8 (C), 95.4 (C), 117.4 (C), 118.8 (CH), 124.1 (CH), 125.1 (CH), 125.2 (C), 129.6 (CH), 129.9 (CH), 132.7 (CH),

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132.8 (CH), 142.1 (C), 146.9 (C), 157.5 (CH), 158.8 (CH), 161.5 (C). IR (ATR) ν: 3035, 2203, 1590, 1513, 1496, 1314, 1288, 818, 756 cm^{-1} HRMS MALDI (matrix DHB) m/z calculated for $C_{54}H_{33}N_7S_3$ $[M+H]^+$ 876.2038, found 876.2051.

Tris-{4-[4-((*E*)-2-quinoxalin-2-yl-vinyl)-phenylethynyl]-phenyl}-amine (3): The title compound was obtained from **8** following the general procedure for Sonogashira cross-coupling reaction and was purified by column chromatography (Al_2O_3, EtOAc). Orange solid (70 mg, 28 %). Mp: 190 °C (dec). ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) : 7,11 (d, 6H, ^3J = 8.7 Hz), 7.42 (d, 3H, ^3J = 16.2 Hz), 7.57 (d, 6H, ^3J = 8.7 Hz), 7.58 (d, 6H, ^3J = 8.4 Hz), 7.68 (d, 6H, ^3J = 8.4 Hz), 7.80-7.72 (m, 6H), 7.88 (d, 3H, ^3J = 16.2 Hz), 8.10-8.06 (m, 6H), 9.05 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) : 89.4 (C), 91.1 (C), 117.9 (C), 124.1 (CH), 124.2 (C), 125.9 (CH), 127.4 (CH), 129.2 (CH), 129.4 (CH), 129.7 (CH), 130.4 (CH), 132.0 (CH), 132.9 (CH), 135.6 (CH), 135.7 (C), 141.6 (C), 142.5 (C), 144.5 (CH), 146.8 (C), 150.4 (C). IR (ATR) ν: 3035, 2207 (C≡C), 1589, 1512, 1493, 1313, 1288, 818, 757 cm^{-1} HRMS MALDI (matrix DHB) m/z calculated for $C_{72}H_{45}N_7$ $[M+H]^+$ 1008.3815, found 1008.3782.

Tris-{4-[5-((*E*)-2-quinoxalin-2-yl-vinyl)-thiophen-2-ylethynyl]-phenyl}-amine (4): The title compound was obtained from **9** following the general procedure for Sonogashira cross-coupling reaction and was purified by column chromatography (SiO_2, Petroleum Ether/EtOAc/NEt_3, 13/6/1) followed by crystallization from MeOH. Red solid (155 mg, 60 %). Mp: 158-160 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) : 7.20 (d, 6H, ^3J = 8.7 Hz), 7.27 (d, 3H, ^3J = 3.4 Hz), 7.30 (d, 3H, ^3J = 3.4 Hz), 7.35 (d, 3H, ^3J = 15.9, Hz), 7.56 (d, 6H, ^3J = 8.7 Hz), 7.88-7.77 (m, 6H), 8.05 (d, 3H, ^3J = 15.9, Hz), 8.17-8.14 (m, 6H), 9.05 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) : 82.9 (C), 95.2 (C), 117.5 (C), 124.1 (CH), 124.6 (C), 124.9 (CH), 128.6 (CH), 129.0 (CH), 129.1 (CH), 129.2 (CH), 129.3 (CH), 130.4 (CH), 132.7 (CH), 132.8 (CH), 141.5 (C), 142.5 (C), 142.7 (C), 144.5 (CH), 146.8 (C), 150.0 (C). IR (ATR) ν:

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3028, 2190 (C≡C), 1618, 1593, 1523, 1497, 1285, 949, 754 cm^{-1} HRMS (ESI/ASAP) m/z calculated for $C_{66}H_{40}N_7S_3$ $[M+H]^+$ 1026.2502, found 1026.2501.

Tris-{4-[4-((*E*)-2-pyrazin-2-yl-vinyl)-phenylethynyl]-phenyl}-amine (5): The title compound was obtained from **10** following the general procedure for Sonogashira cross-coupling reaction and was purified by column chromatography (SiO_2, EtOAc/NEt_3, 19/1) followed by crystallization from MeOH. Yellow solid (50 mg, 23 %). Mp: 110 °C (dec). ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) : 7.10 (d, 6H, ^3J = 8.4 Hz), 7.17 (d, 3H, ^3J = 16.2 Hz), 7.46 (d, 6H, ^3J = 8.4 Hz), 7.53 (d, 6H, ^3J = 8.4 Hz), 7.58 (d, 6H, ^3J = 8.4 Hz), 7.75 (d, 3H, ^3J = 15.9, Hz), 8.42 (broad s, 3H), 8.56 (broad s, 3H), 8.65 (broad s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) : 82.3 (C), 89.9 (C), 117.9 (C), 124.1 (CH), 124.7 (CH), 127.1 (CH), 131.6 (C), 131.9 (CH), 132.0 (CH), 132.9 (CH), 134.4 (CH), 135.8 (C), 143.9 (CH), 144.4 (CH), 146.8 (C), 151.1 (C). IR (ATR) ν: 3035, 2207 (C≡C), 1589, 1512, 1493, 1313, 1288, 818, 757 cm^{-1} HRMS (ESI/ASAP) m/z calculated for $C_{60}H_{40}N_7$ $[M+H]^+$ 858.3340, found 858.3337.

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Supporting Information Available: copies of ^{1}H NMR and ^{13}C NMR spectra for all compounds, plots of emission maxima versus $E_T(30)$, representative CV diagram and correlations. This material is available free of charge via the internet.

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Chart 1.

Scheme 1. Synthesis of bromo-substituted intermediates 6-9.

Scheme 2. Synthesis of compound 10.

Scheme 3. Final Sonogashira cross-coupling ($Pd(PPh_3)_4$, CuI, 1,4-dioxane, iPr_2HN, 92 °C, 12h).

Figure 1: Normalized UV/vis (solid lines) and emission spectra (dashed lines) of compounds 1 and 4.

Figure 2. Normalized emission of compound 2 in different aprotic solvents.

Figure 3. Fluorescence color changes for 3 in various solvents (from left to right: hexane, toluene, dioxane, THF and dichoromethane. Picture was taken in the dark upon irradiation with a hand-held UV lamp (λ_{em} = 366 nm).

Figure 4: Color change of a DCM solution ($c = 10^{-1}$ M) of 4 in the presence of TFA.

Figure 5: UV/vis spectra of 2 in DCM ($c = 6\ 10^{-6}$ M) with and without addition of TFA ($c = 10^{-1}$ M).

Figure 6: Two-photon absorption spectra of the chromophores 1-5 in dichloromethane.

Figure 7: Energy level diagram showing electrochemical (black) and DFT calculated (red) HOMO and LUMO levels of 1-5.

Figure 8: HOMO/HOMO-1 (red) and LUMO/LUMO+1 (blue) localization in 4 and HOMO/LUMO mix in 1-3 and 5.

Table 1. UV/Vis and photoluminescence (PL) data in CH_2Cl_2.

Table 2. Emission solvatochromism of diazine derivatives 1-5 in various aprotic solvents.

Table 3. Two-photon absorption photophysical properties of compounds 1-5 in dichloromethane.

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Table 4. Electrochemical,[a] and DFT calculated data as well as optical gap for chromophores 1-5.

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Compd[a]	UV/vis λ_{max}, nm (ε,$mM^{-1}\cdot cm^{-1}$)	PL λ_{max}, nm	Φ_F[b]	Stokes shift[c] cm^{-1}
1	332 (72.5), 401 (86.0)	577	0.55	7610
2	363sh (56.7) , 422 (89.2)	587	0.58	6660
3	345sh (69.5), 413 (108.2)	630	0.37	8340
4	370sh (60.6), 436 (108.3)	617	0.38	6730
5	339(53.4), 404 (74.5)	551	0.67	6600

[a] All spectra were recorded at room temperature at $c = 1.0$ to 2.0×10^{-5} M for absorption and $c = 1.0 \times$ to 3.0×10^{-6} M for emission. [b] Fluorescence quantum yield (±10%) determined relative to 9,10-bis-phenylethynyl-anthracene in cyclohexane ($\Phi_F = 1.00$).[1] [c] Calculated using less energetic absorption band.

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Compd	Hexane $E_T(30)^a = 31.0$ λ_{max}, nm	Toluene $E_T(30)^a = 33.9$ λ_{max}, nm	Dioxane $E_T(30)^a = 36.0$ λ_{max}, nm	THF $E_T(30)^a = 37.4$ λ_{max}, nm	CH_2Cl_2 $E_T(30)^a = 40.7$ λ_{max}, nm	Acetone $E_T(30)^a = 42.2$ λ_{max}, nm	MeCN $E_T(30)^a = 45.6$ λ_{max}, nm
1	441	463	479	539	577	-[b]	-[b]
2	468, 493	487	501	551	587	618	-[b]
3	458	484	499	576	630	664	-[b]
4	485, 516	508, 535	533	580	617	635	-[b]
5	432	448	461	513	551	581	612

[a] Dimroth–Reichardt polarity parameter,kJ·mol^{-1}. [b] no signal detected

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Compound	λ_{1PA} / nm	λ_{2PA} / nm	δ_{max}/ GM [a]	$\Phi\times\delta_{max}$ / GM
1	401	760	256	141
2	422	800	427	248
3	413	780	239	88
4	436	760	416	158
5	404	740	158	106

[a] The experimental error on 2PA cross section is 15%.

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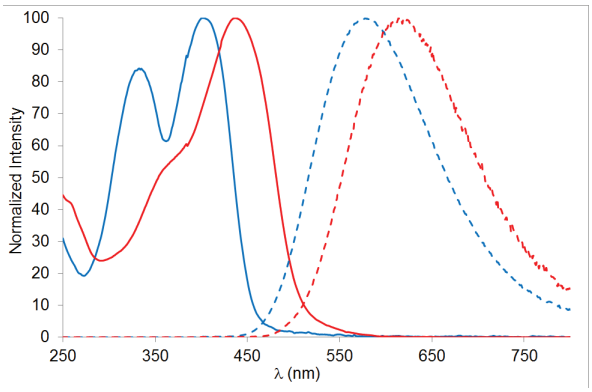
Comp.	$E_{1/2}^{(ox1)}$ / V[a]	$E_{1/2}^{(red1)}$ / V[a]	E_{HOMO} / eV[b]	E_{LUMO} / eV[b]	Eg^{elchem} / eV[c]	$Eg^{optical}$ / eV	E_{HOMO}^{DFT} / eV[f]	E_{LUMO}^{DFT} / eV[f]	Eg^{DFT} / eV[f]	μ_G / D[f]
1	0.61	-1.91	-5.41	-2.89	2.52	2.63	-5.42	-2.72	2.70	3.62
2	-[d]	-1.70	-	-3.10	-	2.53	-5.32	-2.74	2.58	0.08
3	0.63	-1.77	-5.43	-3.03	2.40	2.57	-5.31	-2.77	2.54	4.79
4	0.69[e]	-1.72	-5.49	-3.08	2.41	2.43	-5.23	-2.92	2.31	1.40
5	0.64	-2.02	-5.44	-2.78	2.66	2.71	-5.33	-2.44	2.89	0.48

[a] All potential are given vs. ferrocene; [b] $E_{HOMO/LUMO} = -(E_{1/2(ox1/red1)} + 4.8)$;[1] [c] $Eg = E_{HOMO} - E_{LUMO}$; [d] Undistinguishable wave; [e] Irreversible peak, stand for *E*p; [f] All data were calculated by DFT method HCTH/6-311+G(d)//B3LYP/6-311++G(2d,p).

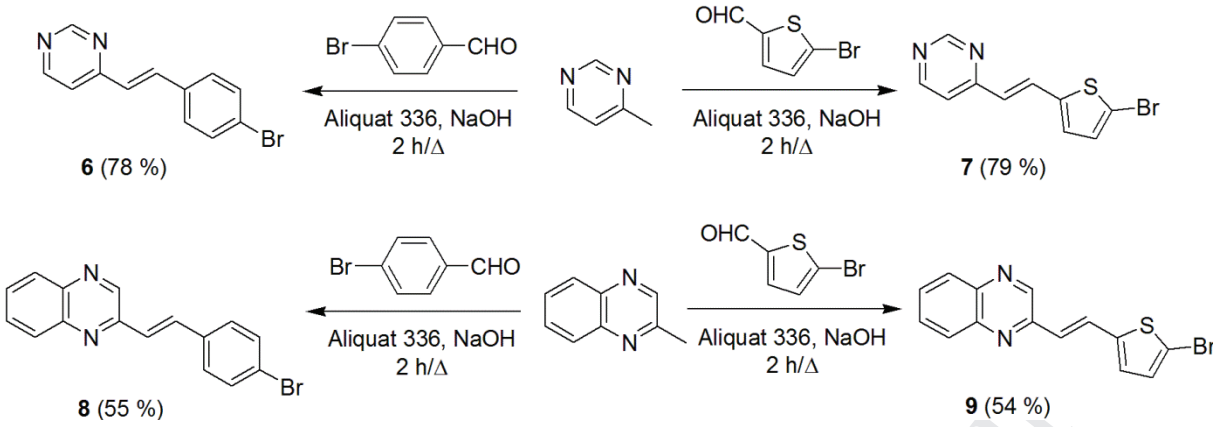
[1] A. A. Isse, A. Gennaro, J. Phys. Chem. B, **2010,** *114*, 7894-7899.

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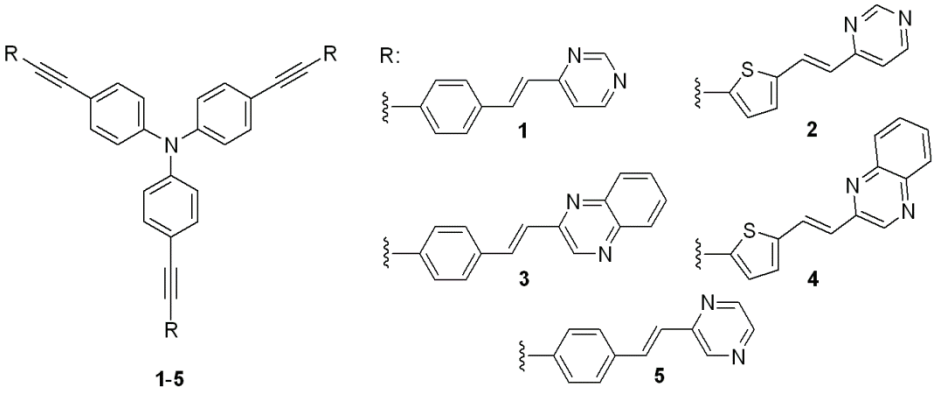
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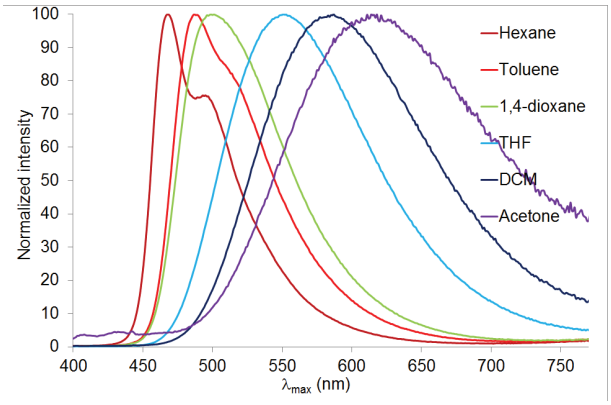


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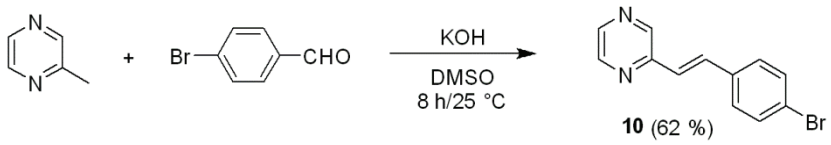


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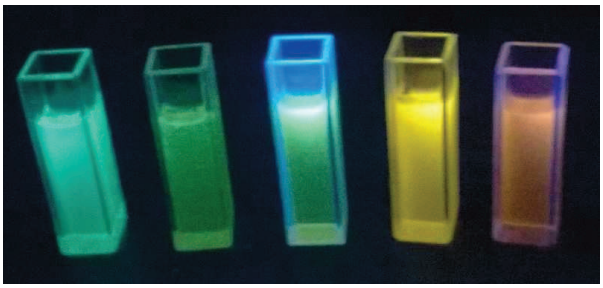


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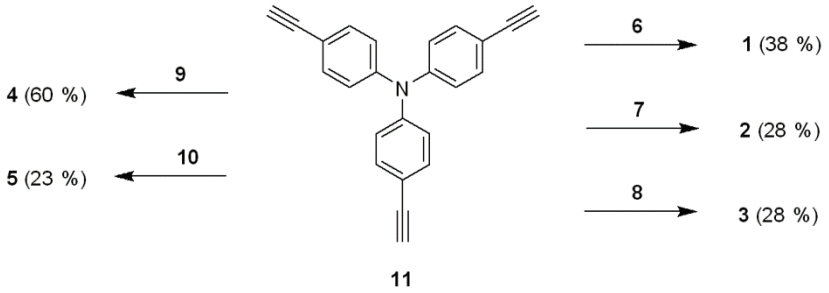


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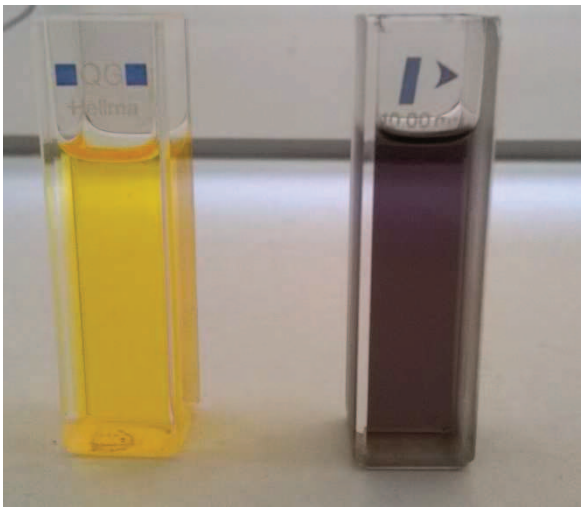


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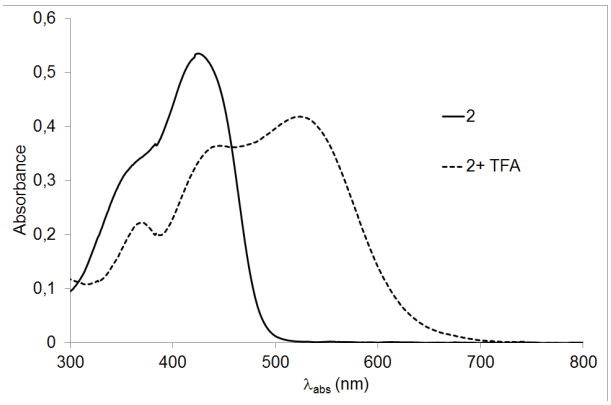
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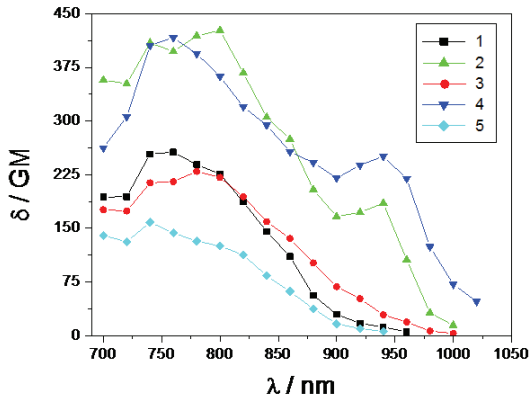


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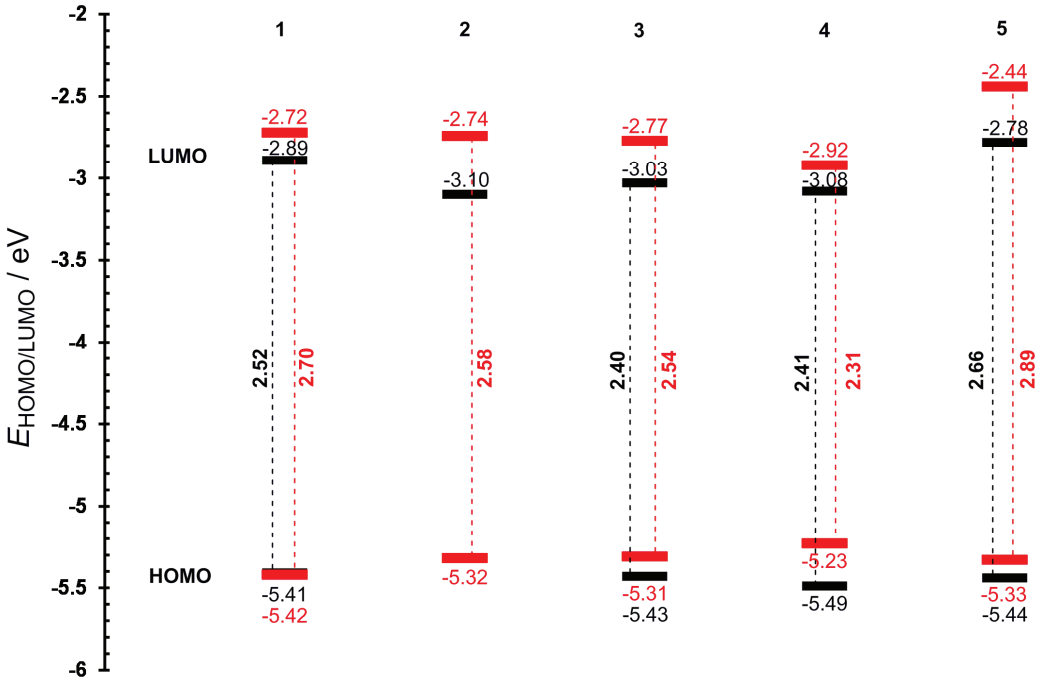
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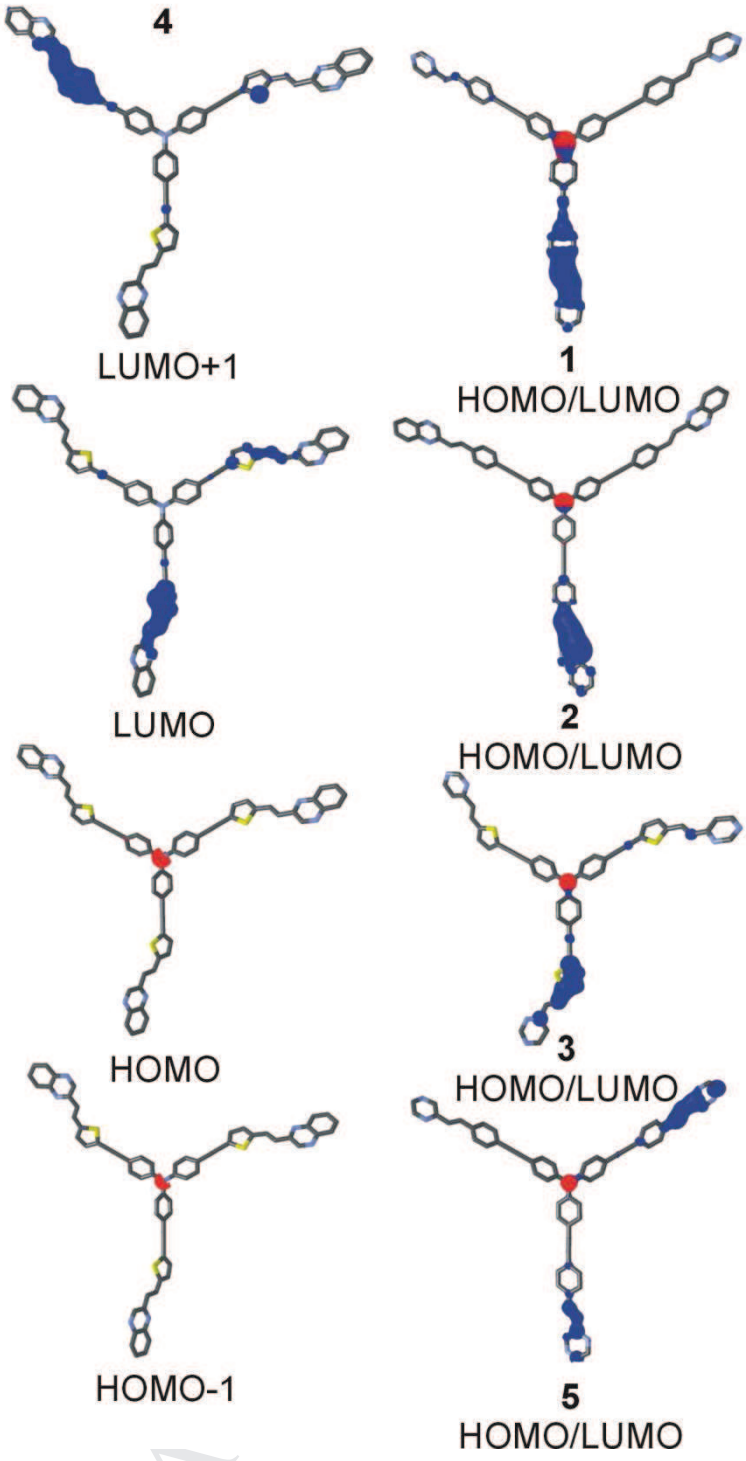
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4
LUMO+1
1
HOMO/LUMO
LUMO
2
HOMO/LUMO
HOMO
3
HOMO/LUMO
HOMO-1
5
HOMO/LUMO

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Octupolar molecules with central triphenylamine and peripheral diazine were prepared.

A strong positive emission solvatochromism is observed.

These materials exhibit two-photon absorption properties.

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SUPPORTING INFORMATION

Star-shaped molecules with triphenylamine core, diazine peripheral groups and extended π-conjugated linkers

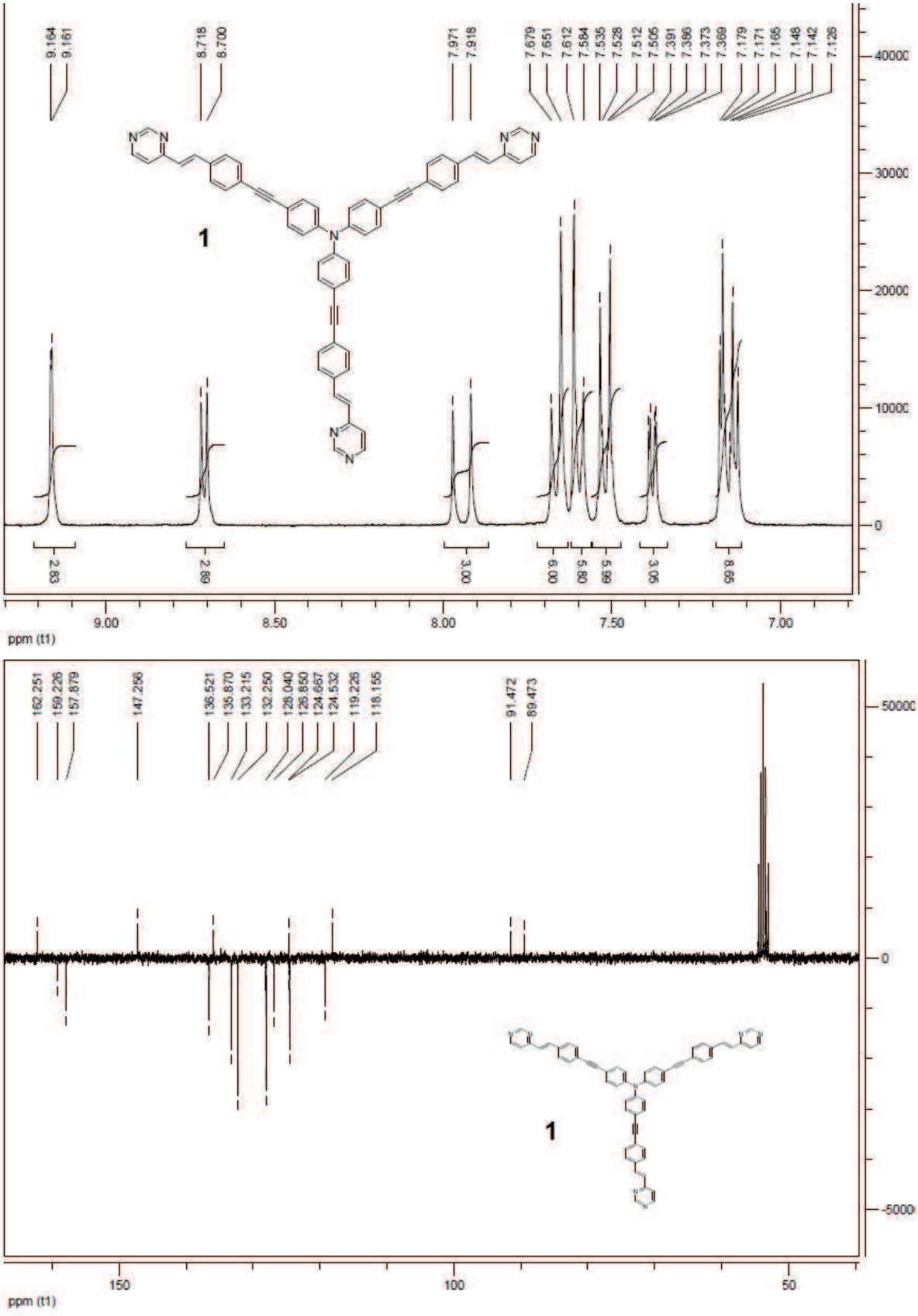
Daniel Cvejn,[a, b] Sylvain Achelle,*[a] Oldřich Pytela,[b] Jean-Pierre Malval,[c] Arnaud Spangenberg,[c] Nolwenn Cabon,[a] Filip Bureš,*[b] and Françoise Robin-le Guen[a]

[a]Institut des Sciences Chimiques de Rennes UMR CNRS 6226, IUT de Lannion, rue Edouard Branly, BP 30219, F22302 Lannion Cedex, France. [b]Institute of Organic Chemistry and Technology, Faculty of Chemical Technology, University of Pardubice, Studentská 573, Pardubice, 53210, Czech Republic. [c]Institut de Science des Matériaux de Mulhouse UMR CNRS 7361, Université de Haute-Alsace 15 rue Jean Starcky, 68057 Mulhouse, France

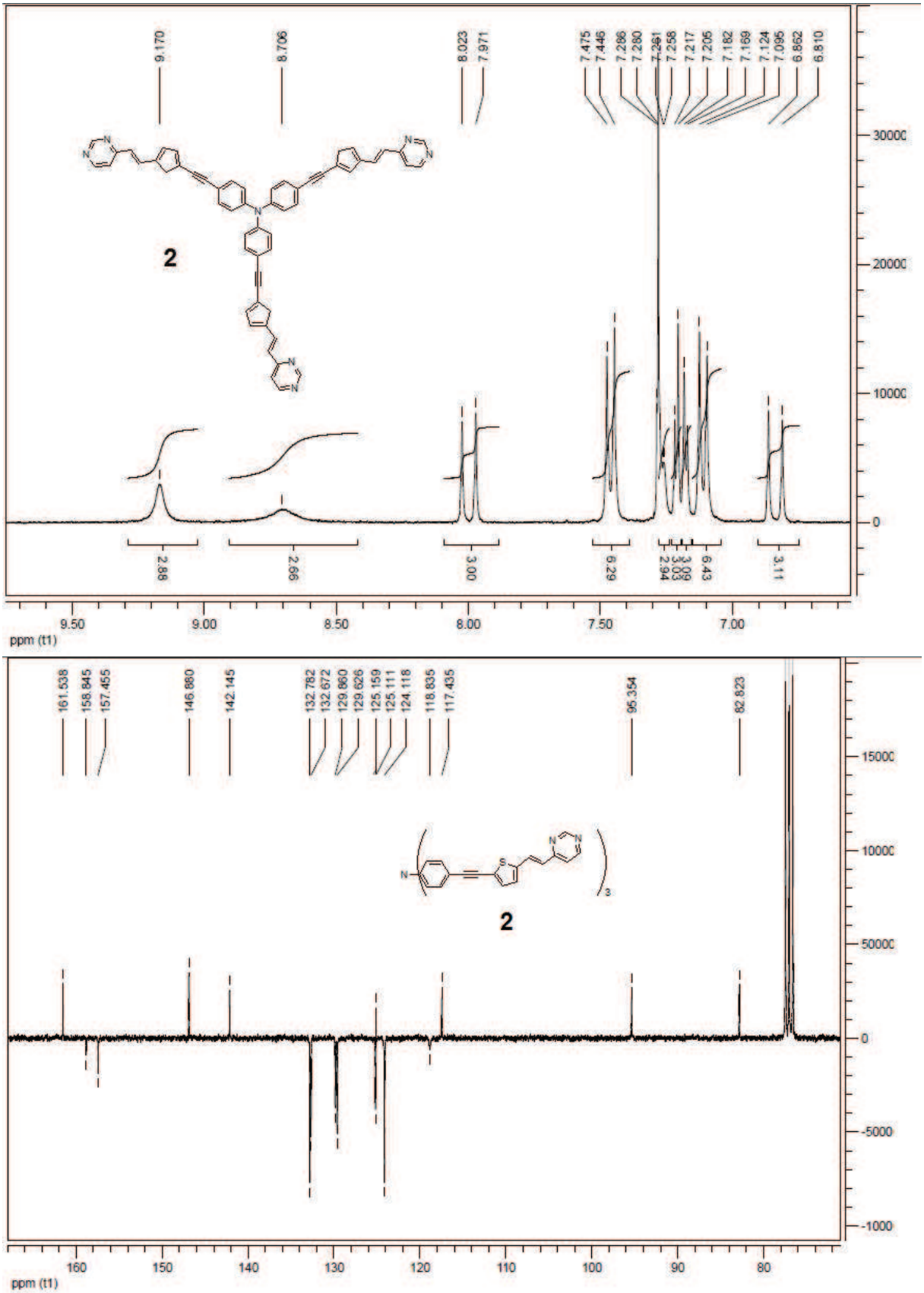
Corresponding authors: *E-mails: sylvain.achelle@univ-rennes1.fr; filip.bures@upce.cz

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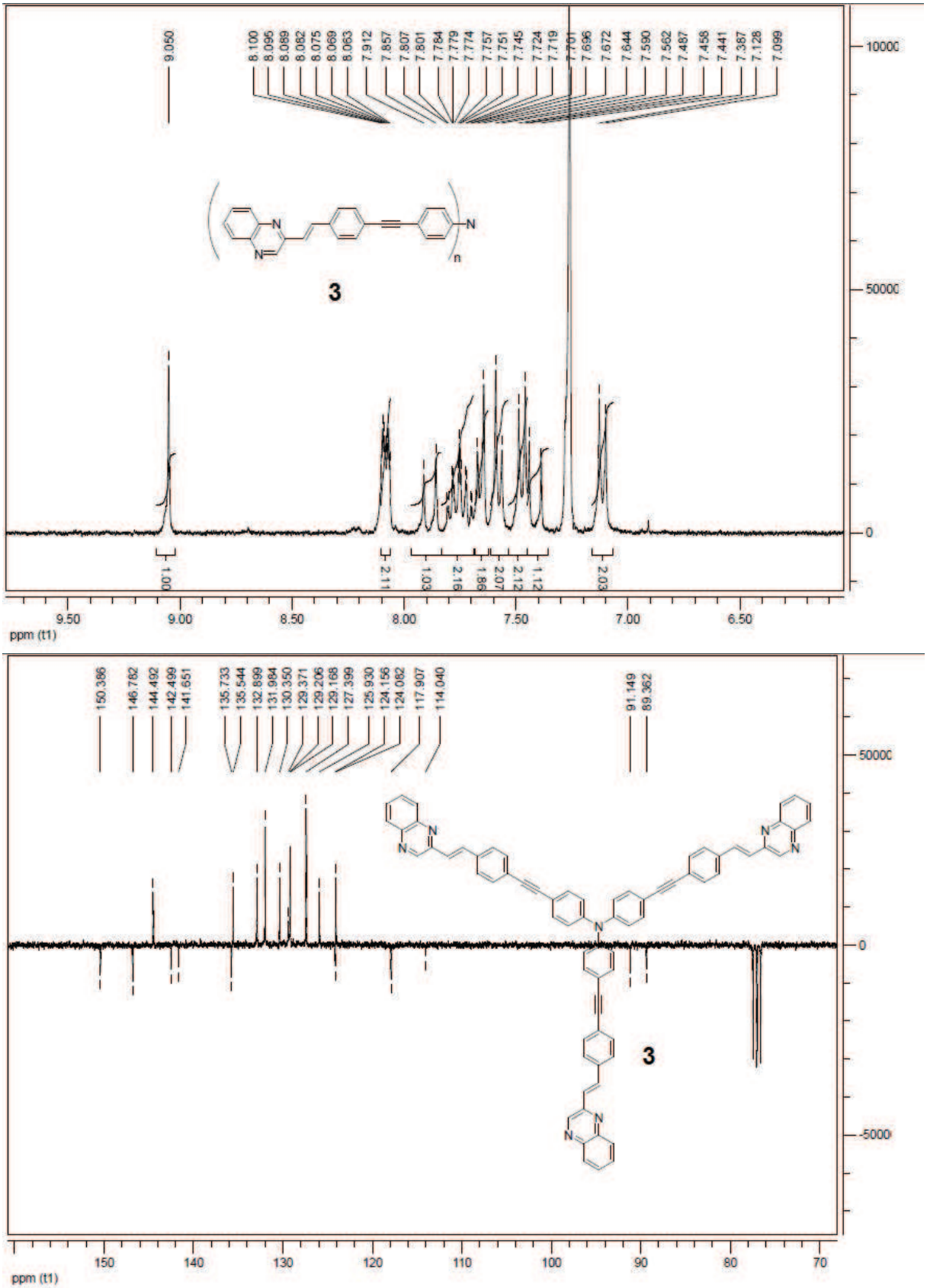
1. NMR spectra for compounds **1-5** (p S2-S6).
2. NMR spectra for compounds **9** and **10** (p S7-S8).
3. UV/Vis and photoluminescence (PL) data of compounds **1-5** in Toluene (p S9).
4. Emission wavelength as a function of $E_T(30)$ for compounds **1- 5** (p S10).
5. Fluorescence color changes for **5** in various solvents (p S11).
6. Representative CV diagram of compound **5**. (p S12)
7. 1PA and 2PA spectra of compounds **1-5** (p S13)
8. DFT calculations (p S16)



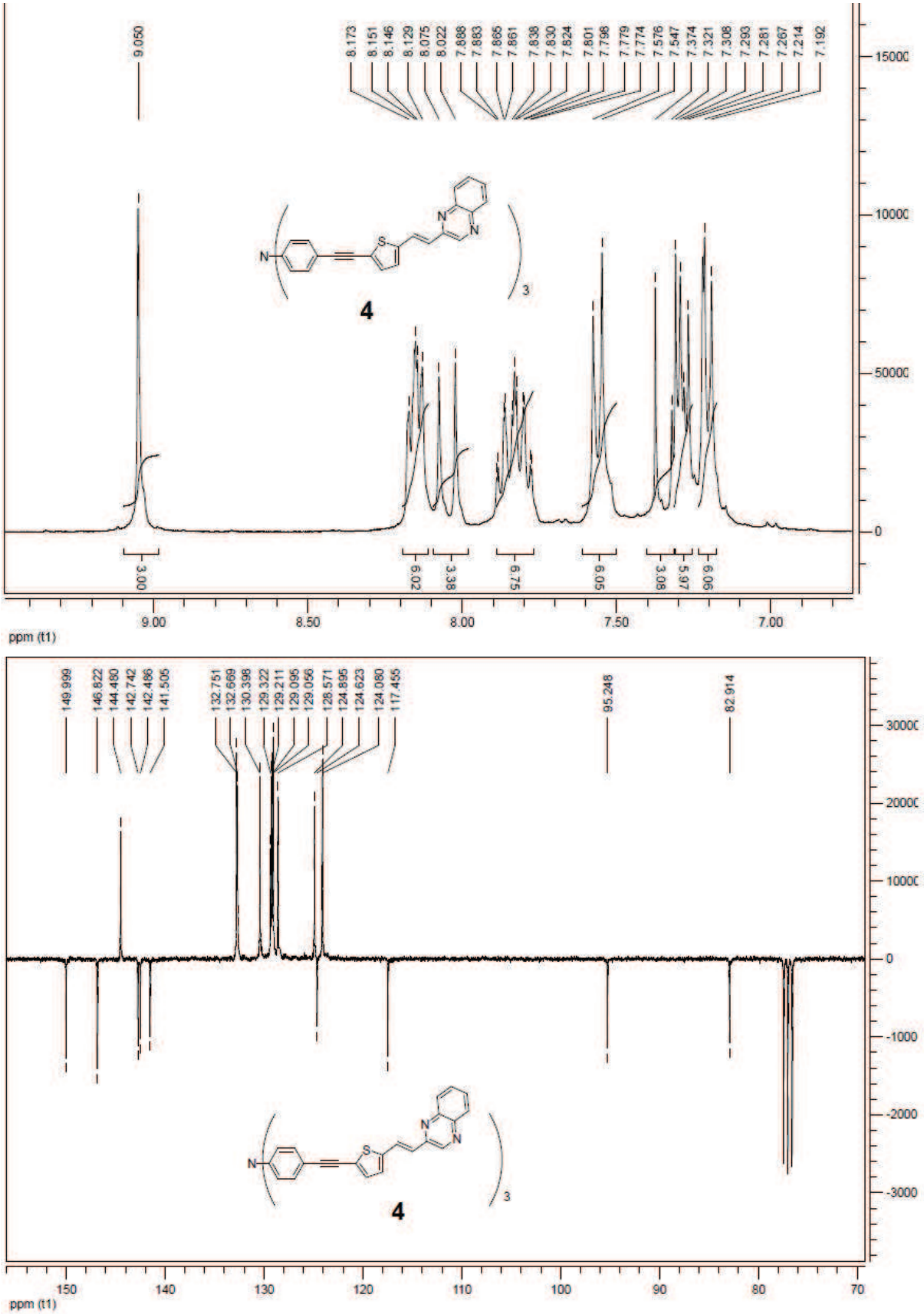
^{1}H and ^{13}C-NMR spectra of chromophore **1** (300/75 MHz, $CDCl_3$).



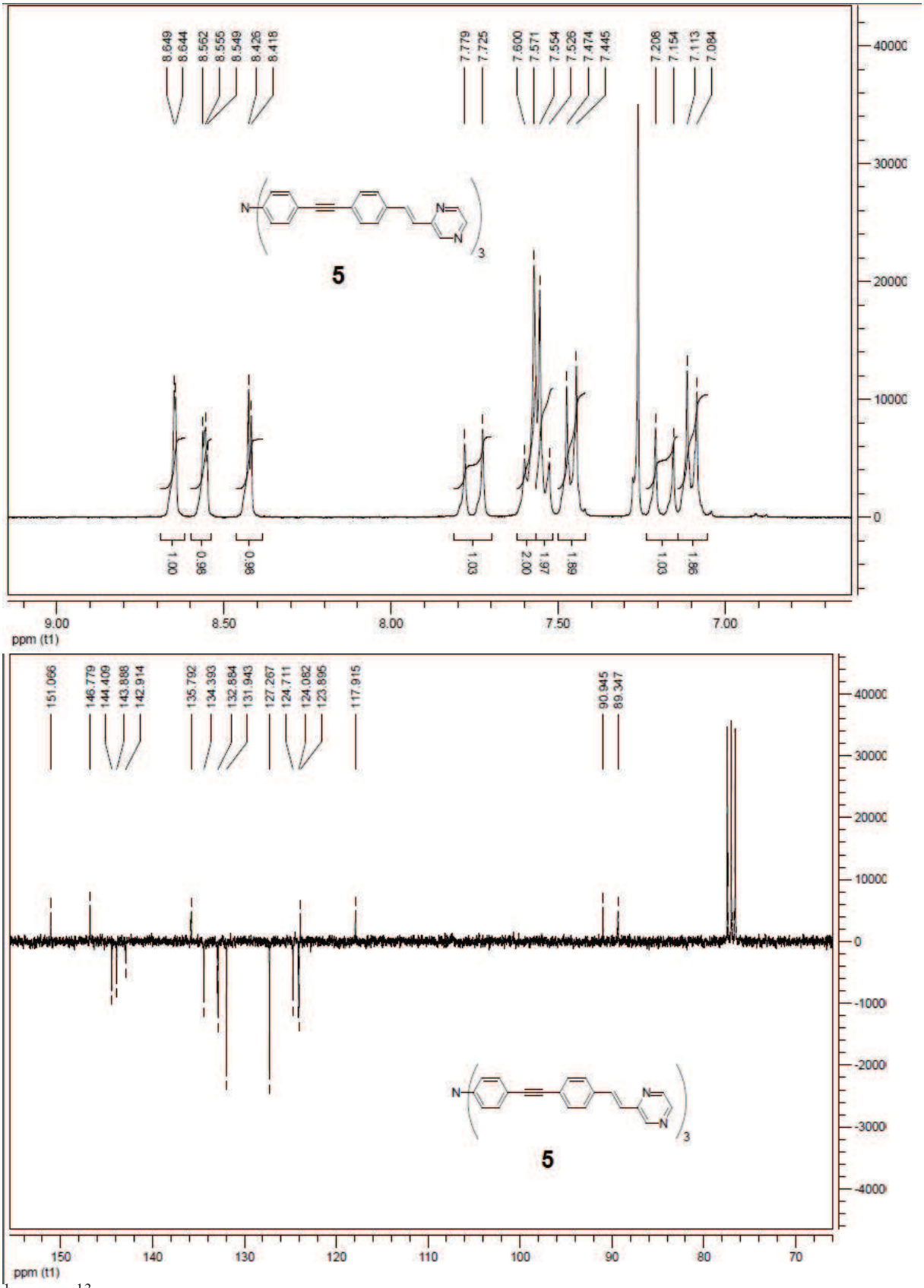
^{1}H and ^{13}C-NMR spectra of chromophore **2** (300/75 MHz, $CDCl_3$).



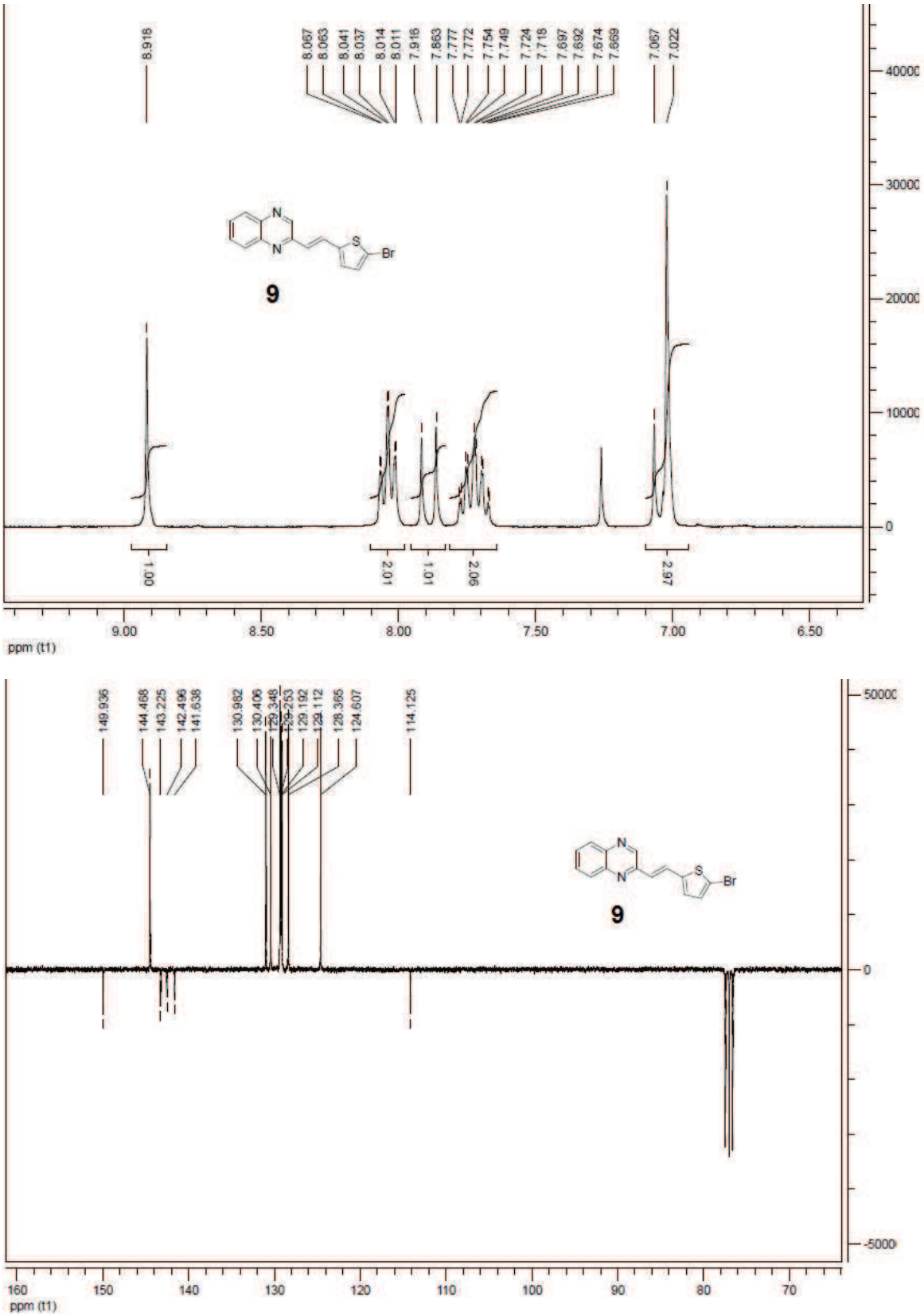
^{1}H and ^{13}C-NMR spectra of chromophore **3** (300/75 MHz, $CDCl_3$).



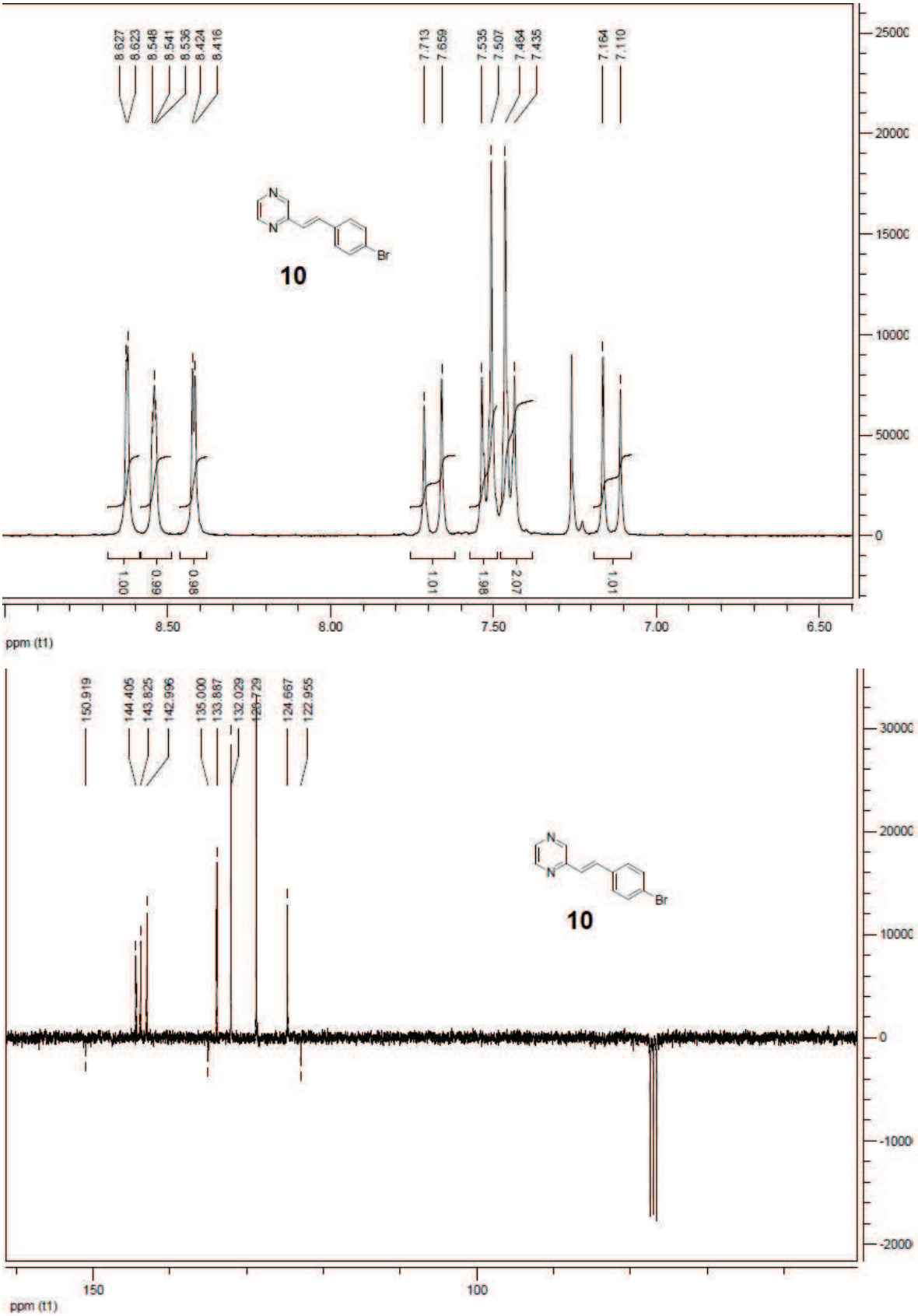
^{1}H and ^{13}C-NMR spectra of chromophore **4** (300/75MHz, $CDCl_3$).



^{1}H and ^{13}C-NMR spectra of chromophore **5** (300/75 MHz, $CDCl_3$).



^{1}H and ^{13}C-NMR spectra of intermediate **9** (300/75 MHz, $CDCl_3$).



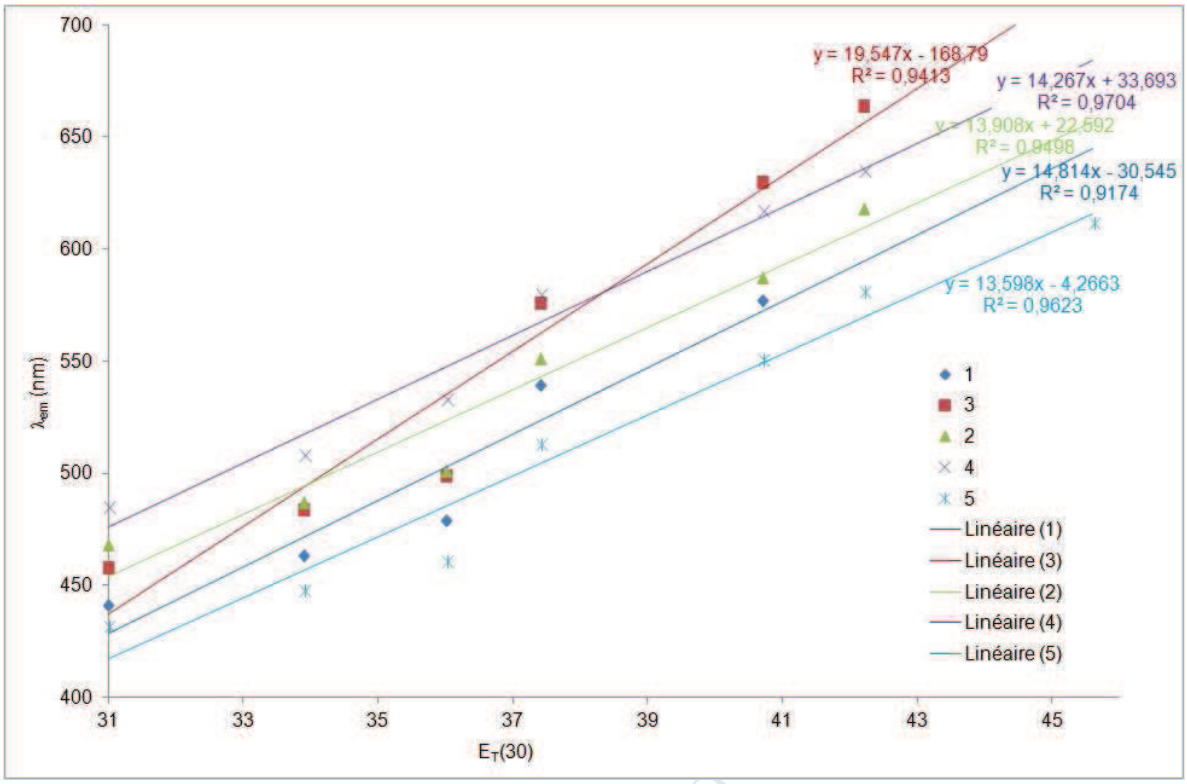
^{1}H and ^{13}C-NMR spectra of intermediate **10** (300/75 MHz, $CDCl_3$).

UV/Vis and photoluminescence (PL) data in Toluene

Compd[a]	UV/vis λ_{max}, nm (ε,$mM^{-1}\cdot cm^{-1}$)	PL λ_{max}, nm	Φ_F[b]	Stokes shift[c] cm^{-1}
1	326 (74.2), 401 (96.8)	463	1.00	3339
2	363 (58.3), 422 (95.1)	487	0.45	3163
3	344 (71.6), 411 (120.9)	484	0.73	3670
4	439 (103.3)	508, 535(sh)	0.51	3094
5	341 (45.4), 397 (65.4)	448	0.67	2867

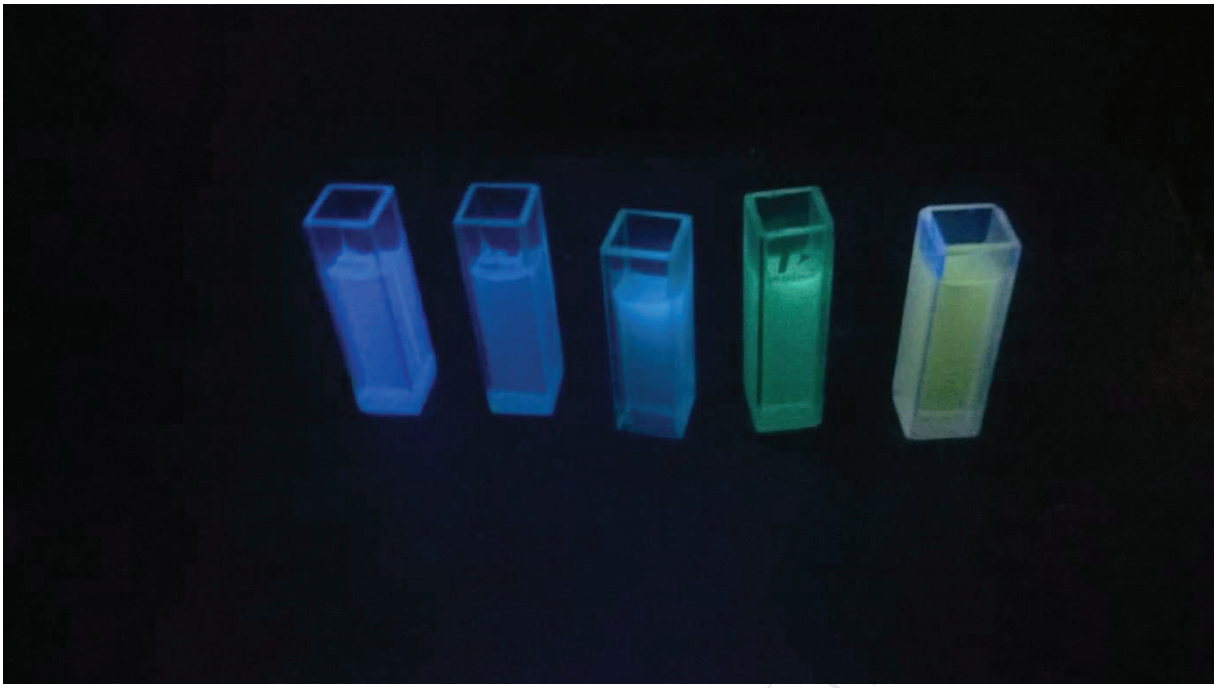
[a] All spectra were recorded at room temperature at $c = 1.0 \times 10^{-5}$ M to 2.0×10^{-5} M for absorption and $c = 1.0 \times 10^{-6}$ M to 3.0×10^{-6} M for emission. [b] Fluorescence quantum yield (±10%) determined relative to 9,10-Bis-phenylethynyl-anthracene in cyclohexane ($\Phi_F = 1.00$).[i] [c] calculated using less energetic absorption band.

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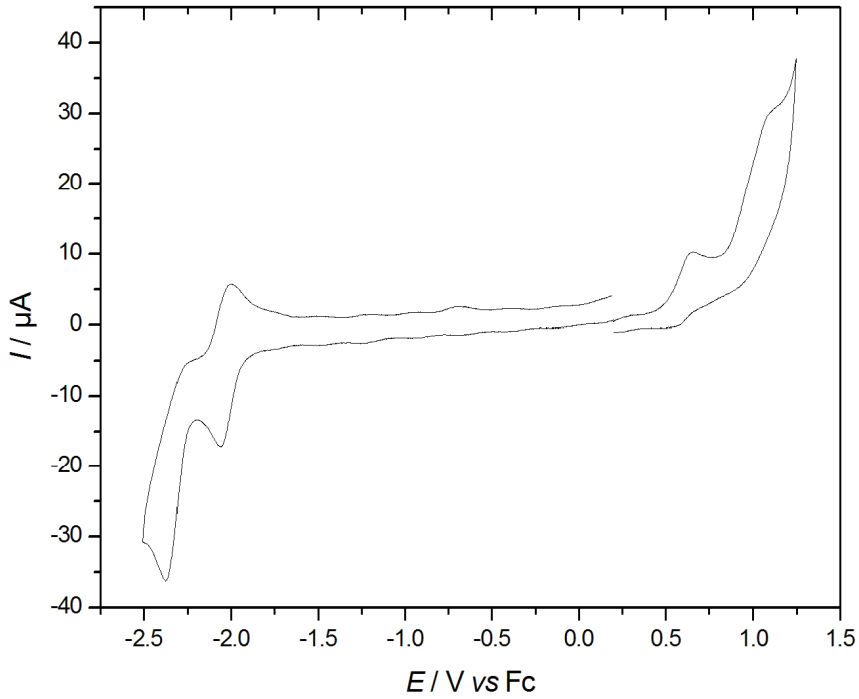
Correlation of the longest-wavelength absorption maxima and $E_T(30)$ parameters.

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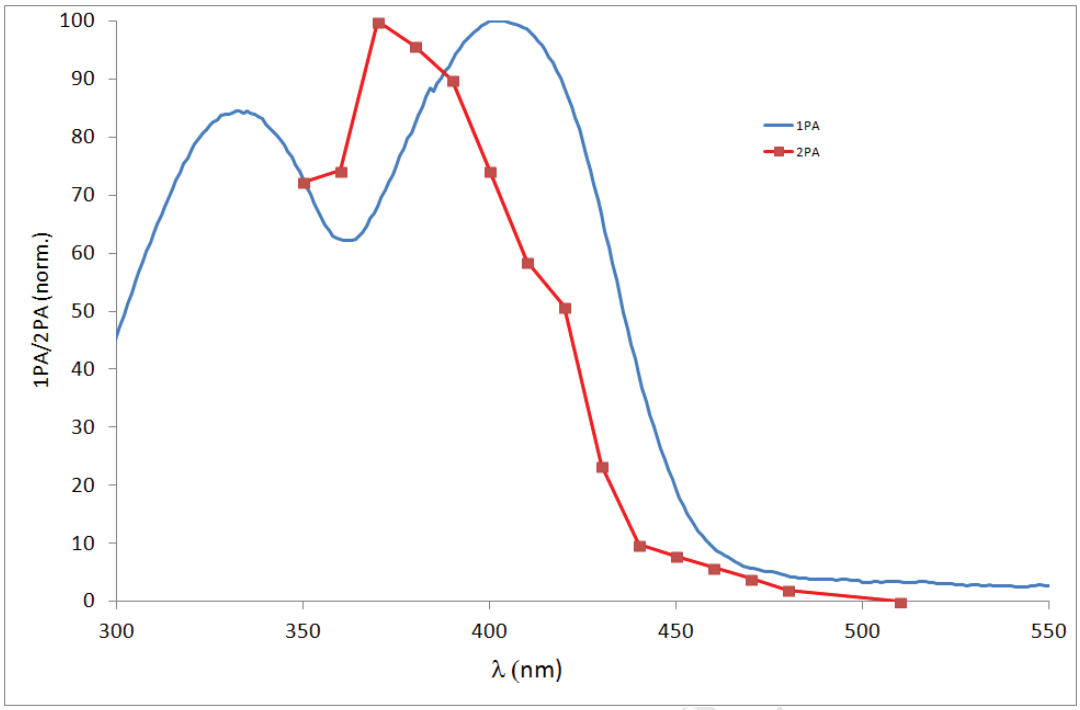
Color of solution of chromophore **5** in various solvents ($c = 10^{-5}$ M) taken under irradiation with a handheld UV lamp (365 nm). From left to right: Hexane, Toluene, dioxane, THF, DCM.

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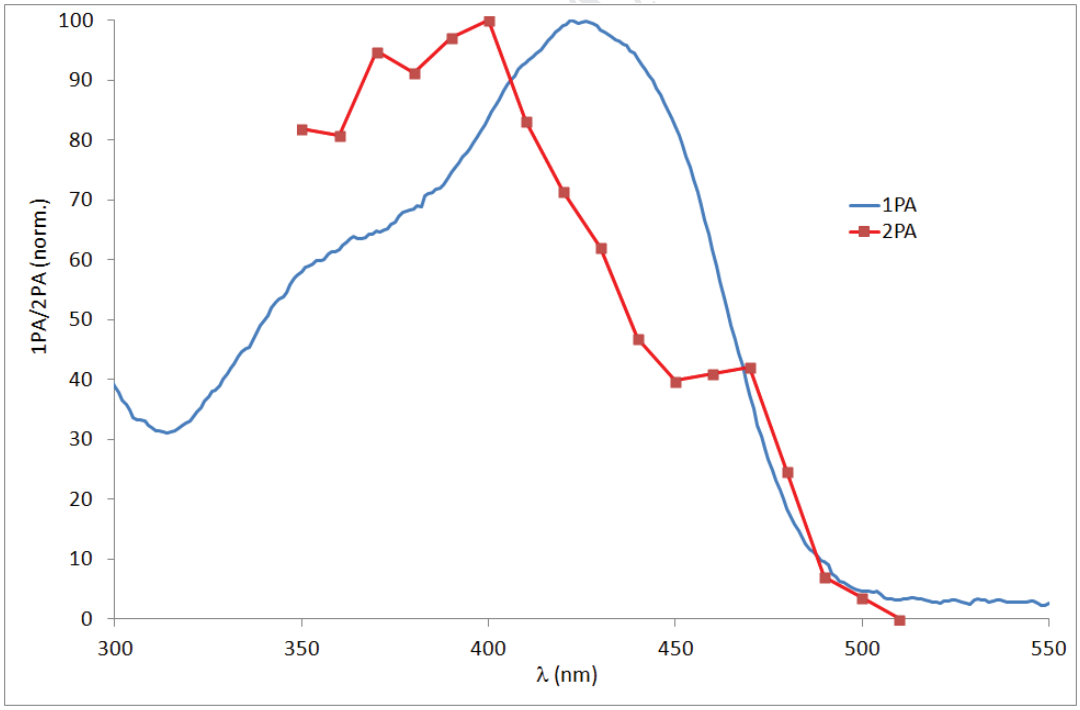


Representative CV diagram of compound **5**.

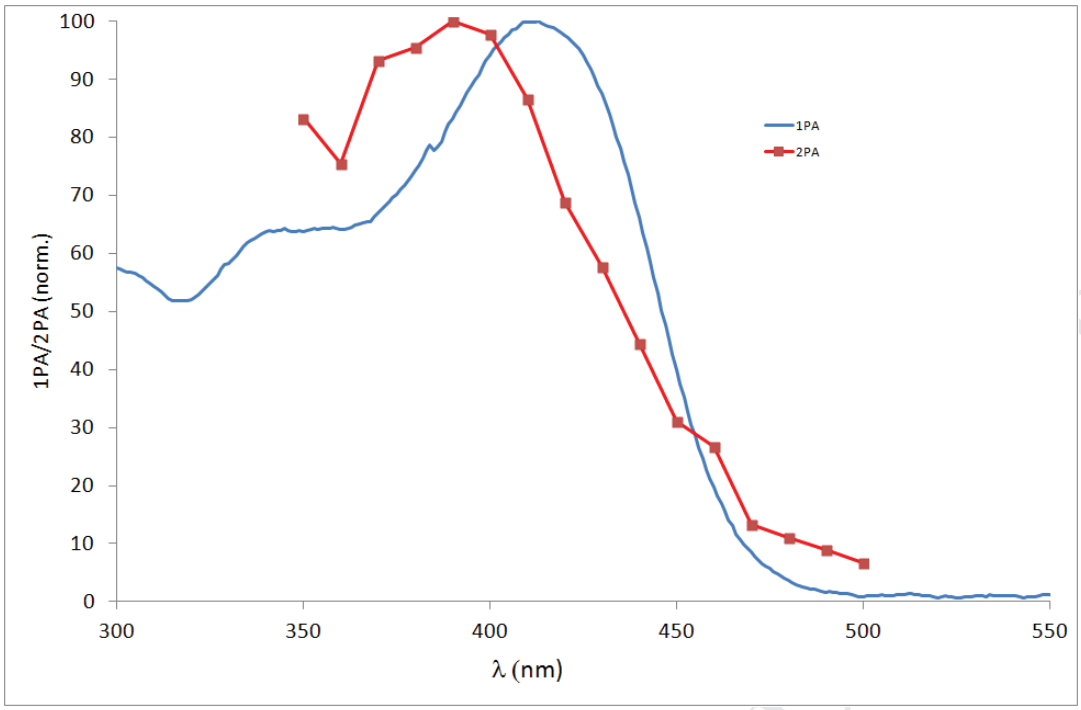
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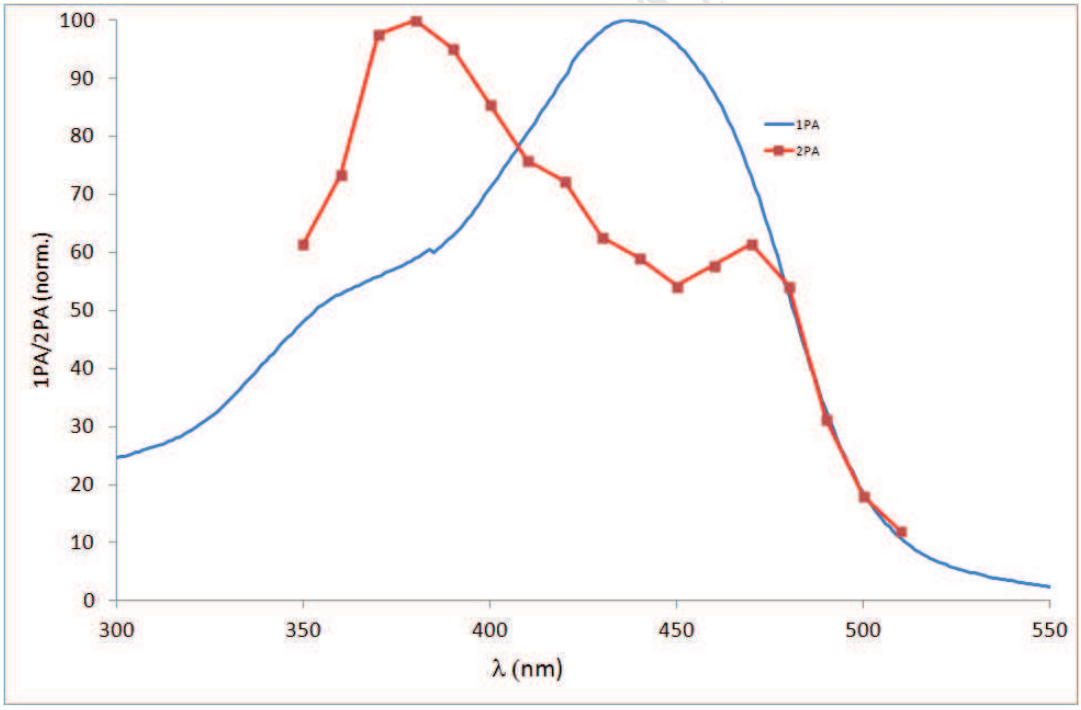
1PA (blue) and 2PA (red) spectra (plotted against half of the excitation wavelength) of **1** in dichloromethane.



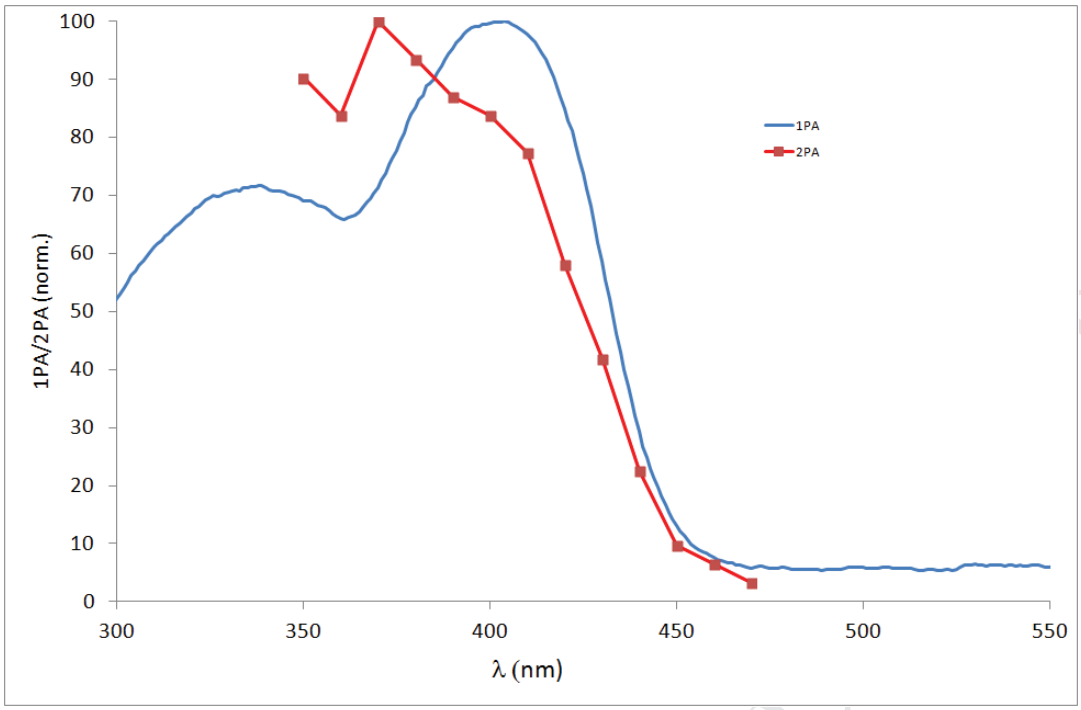
1PA (blue) and 2PA (red) spectra (plotted against half of the excitation wavelength) of **2** in dichloromethane.



1PA (blue) and 2PA (red) spectra (plotted against half of the excitation wavelength) of **3** in dichloromethane.



1PA (blue) and 2PA (red) spectra (plotted against half of the excitation wavelength) of **4** in dichloromethane.

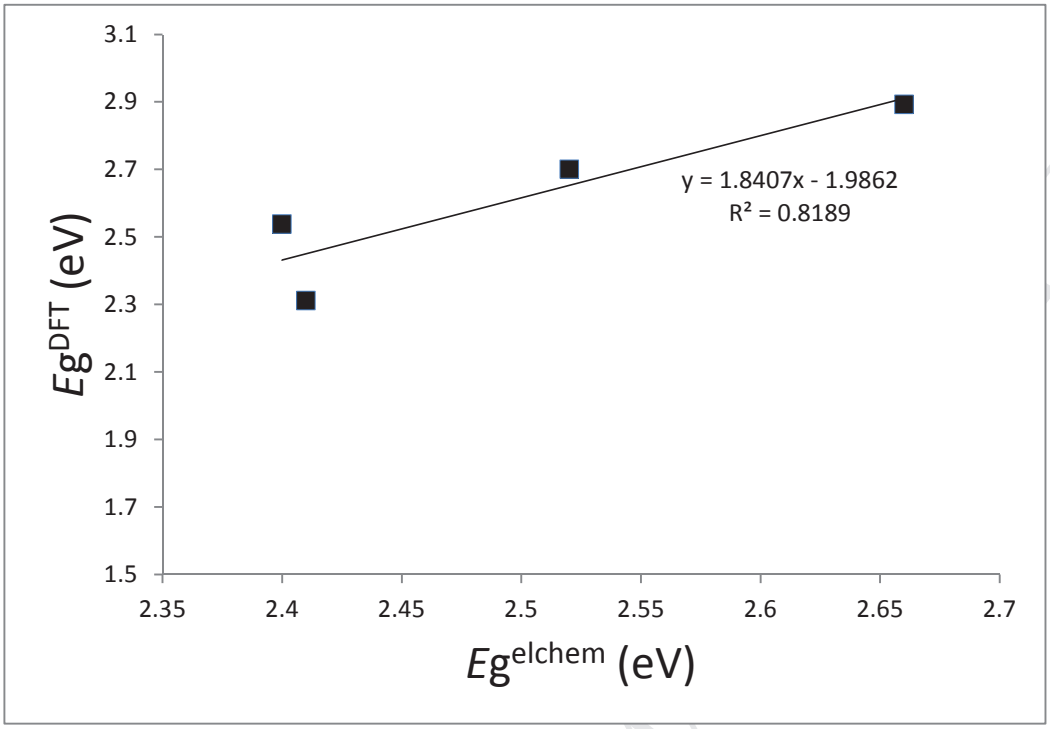


1PA (blue) and 2PA (red) spectra (plotted against half of the excitation wavelength) of **5** in dichloromethane.

ACCEPTED MANUSCRIPT

DFT calculations

All data were calculated by DFT method HCTH/6-311+G(d)//B3LYP/6-311++G(2d,p)



DFT calculated vs. electrochemical gaps *E*g.

ACCEPTED MANUSCRIPT

Chromophore 1

Total energy = -7.329624646E+4 eV, -2.693655307E+3 hartree, -1.690276786E+6 kcal/mol

Cartesian coordinates

N	Atom	X	Y	Z
1	N	0.0000	0.06160	0.0000
2	C	1.40800	0.06160	0.12670
3	C	-0.59430	0.06160	-1.28270
4	C	-0.81370	0.06160	1.15600
5	C	-1.96510	-0.73100	1.23600
6	C	2.19990	0.89360	-0.70230
7	C	2.05290	-0.73100	1.08380
8	C	-1.70820	0.89360	-1.55400
9	C	-0.08790	-0.73100	-2.31980
10	C	-0.49170	0.89360	2.25630
11	C	4.23340	0.06160	0.38230
12	C	-2.44780	0.06160	3.47510
13	C	-1.78560	0.06160	-3.85740
14	C	-1.28760	0.89360	3.38980
15	C	-2.76750	-0.73100	2.36420
16	C	-2.29190	0.89360	-2.81000
17	C	-0.66370	-0.73100	-3.57890
18	C	3.57950	0.89360	-0.57980
19	C	3.43120	-0.73100	1.21460
20	C	11.0813	0.17590	1.16240
21	C	-6.54730	0.17590	9.01550
22	C	-4.53400	0.17590	-10.1779
23	C	8.25440	0.06160	0.81140
24	C	-4.82990	0.06160	6.74280
25	C	-3.42450	0.06160	-7.55430

26	C	-5.35870	0.89360	8.97650
27	C	-6.84740	-0.61810	7.88010
28	C	10.4532	0.89360	0.15260
29	C	-3.40070	-0.61810	-9.87010
30	C	-5.09450	0.89360	-9.12910
31	C	10.2481	-0.61810	1.99000
32	C	9.08020	0.89360	-0.02320
33	C	-4.52000	0.89360	7.87530
34	C	8.87690	-0.61810	1.82260
35	C	-2.86010	-0.61810	-8.59890
36	C	-6.01680	-0.61810	6.77640
37	C	-4.56020	0.89360	-7.85200
38	C	12.5250	0.17590	1.29360
39	C	-7.38280	0.17590	10.2002
40	C	-5.14220	0.17590	-11.4938
41	C	5.63830	0.06160	0.51790
42	C	-3.26770	0.06160	4.62400
43	C	-2.37070	0.06160	-5.14190
44	C	-8.56590	-0.37350	10.4247
45	C	-4.74510	-0.37350	-12.6306
46	C	13.3110	-0.37350	2.20600
47	C	-5.41700	-0.17590	-13.9148
48	C	-9.34210	-0.17590	11.6486
49	C	14.7591	-0.17590	2.26620
50	C	6.84760	0.06160	0.65540
51	C	-2.85630	0.06160	-6.25790
52	C	-3.99140	0.06160	5.60260
53	H	0.38880	1.52800	2.21630
54	H	-2.22790	-1.36700	0.40320

55	H	-2.11370	1.52800	-0.77150
56	H	0.76470	-1.36700	-2.13100
57	H	1.72500	1.52800	-1.44480
58	H	1.46320	-1.36700	1.72780
59	C	-10.5680	-0.89360	11.7990
60	C	-4.93420	-0.89360	-15.0517
61	C	15.5022	-0.89360	3.25270
62	H	-3.14690	1.52800	-2.99920
63	H	-0.25850	-1.36700	-4.36390
64	H	4.17090	1.52800	-1.22570
65	H	3.90850	-1.36700	1.95810
66	H	-1.02400	1.52800	4.22490
67	H	-3.65000	-1.36700	2.40580
68	C	-5.62200	-0.73100	-16.2435
69	C	-11.2562	-0.73100	12.9905
70	C	16.8783	-0.73100	3.25290
71	N	-8.87700	0.61810	12.6483
72	N	-6.51530	0.61810	-14.0119
73	N	15.3923	0.61810	1.36350
74	C	-9.62670	0.61810	13.7390
75	C	16.7116	0.61810	1.46750
76	C	-7.08490	0.61810	-15.2065
77	H	10.7354	-1.24610	2.74960
78	H	11.0662	1.52800	-0.50520
79	H	-5.09560	1.52800	9.83620
80	H	-7.74900	-1.24610	7.92230
81	H	-5.97060	1.52800	-9.33100
82	H	-2.98650	-1.24610	-10.6720
83	H	8.30490	-1.36700	2.47770

84	H	-2.00670	-1.36700	-8.43110
85	H	-5.01460	1.52800	-7.06690
86	H	8.62740	1.52800	-0.80940
87	H	-3.61280	1.52800	7.87620
88	H	-6.29820	-1.36700	5.95340
89	H	-6.02420	0.89360	-11.5724
90	H	13.0341	0.89360	0.56910
91	H	-7.00990	0.89360	11.0033
92	H	-9.00580	-1.01850	9.66740
93	H	12.8751	-1.01850	2.96550
94	H	-3.86930	-1.01850	-12.6329
95	N	17.5107	0.06160	2.36270
96	N	-6.70920	0.06160	-16.3461
97	N	-10.8015	0.06160	13.9834
98	H	-10.9667	-1.52800	11.0113
99	H	-4.05270	-1.52800	-15.0031
100	H	15.0194	-1.52800	3.99180
101	H	-12.2125	-1.24610	13.1621
102	H	-5.29250	-1.24610	-17.1574
103	H	17.5049	-1.24610	3.99530
104	H	-9.23760	1.24610	14.5368
105	H	-7.97040	1.24610	-15.2684
106	H	17.2080	1.24610	0.73160

ACCEPTED MANUSCRIPT

Chromophore 2

Total energy = -8.584017972E+4 eV, -3.154647978E+3 hartree, -1.979551070E+6 kcal/mol

Cartesian coordinates

N	Atom	X	Y	Z
1	C	11.1057	-0.42310	0.78000
2	C	-6.22840	-0.42310	9.22780
3	C	-4.87730	-0.42310	-10.0079
4	N	16.9412	-0.42310	0.95550
5	N	-7.64310	-0.42310	-15.1492
6	N	-9.29810	-0.42310	14.1938
7	C	-8.91120	0.31700	11.9341
8	C	-5.87970	0.31700	-13.6844
9	C	14.7909	0.31700	1.75030
10	C	8.26830	-0.54890	0.56070
11	C	-4.61970	-0.54890	6.88020
12	C	-3.64850	-0.54890	-7.44090
13	H	-4.51710	2.54710	-16.6243
14	H	16.6556	2.54710	4.40020
15	H	-12.1385	2.54710	12.2241
16	H	-4.84470	-1.88800	9.99410
17	H	-7.37630	1.04330	8.10940
18	H	-6.23280	-1.88800	-9.19270
19	H	-3.33480	1.04330	-10.4428
20	H	10.7111	1.04330	2.33340
21	H	11.0775	-1.88800	-0.80140
22	H	-5.58190	2.54710	-18.8718
23	H	-13.5525	2.54710	14.2700
24	H	19.1344	2.54710	4.60180
25	C	-1.73960	-1.46570	-1.53310

26	C	2.19750	-1.46570	-0.73990
27	C	-0.13360	0.16980	-2.29840
28	C	2.05720	0.16980	1.03350
29	C	-1.92370	0.16980	1.26480
30	C	-0.45800	-1.46570	2.27310
31	C	-5.21410	0.31700	-12.3922
32	C	13.3390	0.31700	1.68060
33	C	-8.12490	0.31700	10.7116
34	C	-4.31810	-1.29320	8.00440
35	C	-5.74490	0.35230	6.95850
36	C	-4.77290	-1.29320	-7.74180
37	C	-3.15380	0.35230	-8.45450
38	C	9.09100	-1.29320	-0.26260
39	C	8.89870	0.35230	1.49600
40	H	15.2029	-1.04330	0.12680
41	H	-7.71120	-1.04330	13.1027
42	H	-7.49170	-1.04330	-13.2295
43	C	-5.93860	1.04330	-15.8298
44	C	-10.7397	1.04330	13.0579
45	C	16.6783	1.04330	2.77200
46	C	-0.79040	-0.67560	1.17190
47	C	-0.61970	-0.67560	-1.27050
48	C	1.41010	-0.67560	0.09860
49	C	-3.03410	-0.54890	-6.17250
50	C	-3.82850	-0.54890	5.71390
51	C	6.86260	-0.54890	0.45860
52	C	-11.2128	0.42310	15.3576
53	C	18.9065	0.42310	2.03180
54	C	-7.69370	0.42310	-17.3894

55	H	3.91870	0.82250	1.85000
56	H	-0.35720	0.82250	-4.31870
57	H	-3.21550	-2.10960	-2.95710
58	H	-3.56150	0.82250	2.46860
59	H	4.16870	-2.10960	-1.30620
60	H	-0.95320	-2.10960	4.26330
61	C	-8.58860	-0.42310	13.0954
62	C	15.6352	-0.42310	0.89020
63	C	-7.04670	-0.42310	-13.9856
64	C	-5.10340	-1.29320	9.14240
65	C	-6.52320	0.42310	8.09840
66	C	-3.75180	0.42310	-9.69840
67	C	10.2750	0.42310	1.60010
68	C	10.4692	-1.29320	-0.15150
69	C	-5.36580	-1.29320	-8.99090
70	C	17.2944	1.88800	3.74760
71	C	-5.40170	1.88800	-16.8512
72	C	-11.8927	1.88800	13.1036
73	C	-7.10280	0.42310	-16.1093
74	C	-10.3997	0.42310	14.2059
75	C	17.5025	0.42310	1.90350
76	N	-5.34520	1.04330	-14.6141
77	N	15.3288	1.04330	2.67800
78	N	-9.98360	1.04330	11.9361
79	H	13.0347	-1.04330	0.12860
80	H	-6.62870	-1.04330	11.2241
81	H	-6.40600	-1.04330	-11.3527
82	C	-12.3282	1.29320	15.3721
83	C	19.4767	1.29320	2.99050

84	C	-7.14850	1.29320	-18.3626
85	N	0.0000	-0.67560	0.0000
86	H	0.40830	-2.10960	2.21940
87	H	-2.20640	0.82250	0.43310
88	H	0.72810	0.82250	-2.12730
89	H	1.71790	-2.10960	-1.46330
90	H	1.47820	0.82250	1.69430
91	H	-2.12620	-2.10960	-0.75610
92	C	-2.69500	0.16980	2.41410
93	C	3.43820	0.16980	1.12690
94	C	3.57900	-1.46570	-0.65290
95	C	-0.74310	0.16980	-3.54100
96	C	-2.35490	-1.46570	-2.77310
97	C	-1.22410	-1.46570	3.42590
98	H	-7.60440	1.29320	-19.3482
99	H	-12.9538	1.29320	16.2597
100	H	20.5582	1.29320	3.08850
101	C	-5.54700	-0.42310	-11.2970
102	C	12.5570	-0.42310	0.84460
103	C	-7.01000	-0.42310	10.4523
104	H	-10.9332	-0.16980	16.2168
105	H	-8.57760	-0.16980	-17.5769
106	H	19.5108	-0.16980	1.36000
107	C	-12.6681	1.99770	14.2403
108	C	18.6665	1.99770	3.85080
109	C	-5.99840	1.99770	-18.0911
110	C	-1.87270	-0.54890	-3.81130
111	C	4.23700	-0.54890	0.28380
112	C	-2.36430	-0.54890	3.52740

113	C	5.64470	-0.54890	0.37510
114	C	-3.14720	-0.54890	4.70090
115	C	-2.49750	-0.54890	-5.07600
116	H	12.8862	1.04330	2.40900
117	H	-4.35690	1.04330	-12.3643
118	H	-8.52930	1.04330	9.95530
119	H	8.63270	-1.92460	-0.99140
120	H	-2.30470	1.04330	-8.30820
121	H	8.34750	1.04330	2.15820
122	H	-6.04280	1.04330	6.15000
123	H	-5.17490	-1.92460	-6.98050
124	H	-3.45780	-1.92460	7.97180

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Chromophore 3

Total energy = -9.947637839E+4 eV, -3.655781674E+3 hartree, -2.294013968E+6 kcal/mol

Cartesian coordinates

N	Atom	X	Y	Z
1	N	0.0000	-0.50690	0.0000
2	C	1.04530	-0.50690	-0.94970
3	C	0.29980	-0.50690	1.38010
4	C	-1.34510	-0.50690	-0.43040
5	C	0.97380	0.30800	-2.10120
6	C	1.33280	0.30800	1.89390
7	C	2.17700	-1.32090	-0.77660
8	C	-0.41590	-1.32090	2.27360
9	C	-2.30660	0.30800	0.20730
10	C	-1.76100	-1.32090	-1.49700
11	C	0.90770	-0.50690	4.14720
12	C	3.13770	-0.50690	-2.85970
13	C	-4.04540	-0.50690	-1.28750
14	C	-3.07270	-1.32090	-1.92000
15	C	1.64190	0.30800	3.24590
16	C	-0.12650	-1.32090	3.62100
17	C	1.99010	0.30800	-3.04490
18	C	-3.63200	0.30800	-0.20110
19	C	3.19910	-1.32090	-1.70100
20	C	-10.4010	-0.30800	-2.59950
21	C	2.94930	-0.30800	10.3072
22	C	7.45170	-0.30800	-7.70780
23	C	6.09540	-0.50690	-5.60620
24	C	-7.90280	-0.50690	-2.47570
25	C	1.80740	-0.50690	8.08190

26	C	8.08080	-1.08190	-6.69290
27	C	1.75580	-1.08190	10.3447
28	C	-9.83660	-1.08190	-3.65180
29	C	8.01400	-0.00110	-8.96740
30	C	-11.7730	-0.00110	-2.45670
31	C	3.75900	-0.00110	11.4240
32	C	-8.45020	-1.32090	-3.56230
33	C	7.31020	-1.32090	-5.53700
34	C	1.14010	-1.32090	9.09930
35	C	1.21890	-0.50690	5.52050
36	C	4.17140	-0.50690	-3.81580
37	C	-5.39030	-0.50690	-1.70460
38	S	-9.13540	0.17990	-1.52360
39	S	5.88720	0.17990	-7.14970
40	S	3.24820	0.17990	8.67330
41	C	4.91780	0.50690	11.4192
42	C	7.43040	0.50690	-9.96850
43	C	-12.3482	0.50690	-1.45060
44	C	8.00360	1.08190	-11.2685
45	C	5.75700	1.08190	12.5656
46	C	-13.7606	1.08190	-1.29710
47	C	5.05730	-0.50690	-4.65840
48	C	1.50560	-0.50690	6.70900
49	C	-6.56300	-0.50690	-2.05060
50	H	1.93090	1.08190	1.21720
51	H	-1.22960	-1.98330	1.90980
52	H	-1.03910	-1.98330	-2.01980
53	H	2.26880	-1.98330	0.11000
54	H	-2.01950	1.08190	1.06360

55	H	0.08860	1.08190	-2.28080
56	H	-3.37530	-1.98330	-2.75080
57	H	-4.35960	0.97400	0.30190
58	H	-0.69460	-1.98330	4.29850
59	H	2.44120	0.97400	3.62460
60	H	4.06990	-1.98330	-1.54770
61	H	1.91840	0.97400	-3.92640
62	C	-14.7706	0.50690	-2.20340
63	C	5.47710	0.50690	13.8935
64	C	9.29360	0.50690	-11.6900
65	C	9.67980	1.08190	-12.9683
66	C	6.39100	1.08190	14.8671
67	C	-16.0708	1.08190	-1.89880
68	N	-14.0856	1.68570	-0.18160
69	N	7.20000	1.68570	-12.1077
70	N	6.88550	1.68570	12.2893
71	C	-15.3695	1.98330	-0.00440
72	C	7.68850	1.98330	-13.3082
73	C	7.68090	1.98330	13.3126
74	H	-10.4490	-1.50800	-4.44160
75	H	1.37800	-1.50800	11.2699
76	H	9.07100	-1.50800	-6.82830
77	H	7.62470	-1.68570	-4.66120
78	H	0.22430	-1.68570	8.93380
79	H	-7.84900	-1.68570	-4.27260
80	H	-12.4041	-0.50690	-3.24540
81	H	9.01260	-0.50690	-9.11950
82	H	3.39140	-0.50690	12.3649
83	N	-16.3999	1.68570	-0.79580

84	N	8.88910	1.68570	-13.8048
85	N	7.51080	1.68570	14.6006
86	H	-11.7344	1.08190	-0.64480
87	H	6.42560	1.08190	-9.83990
88	H	5.30870	1.08190	10.4847
89	H	-14.5606	-0.00110	-3.11380
90	H	9.97690	-0.00110	-11.0529
91	H	4.58360	-0.00110	14.1667
92	H	-16.8916	0.73260	-2.56600
93	H	10.6680	0.73260	-13.3455
94	H	6.22350	0.73260	15.9116
95	H	-15.6099	2.53740	0.90260
96	H	7.02330	2.53740	-13.9699
97	H	8.58660	2.53740	13.0673

ACCEPTED MANUSCRIPT

Chromophore 4

Total energy = -1.120198022E+5 eV, -4.116755622E+3 hartree, -2.583276503E+6 kcal/mol

Cartesian coordinates

N	Atom	X	Y	Z
1	N	0.0000	-1.16430	0.0000
2	C	1.14620	-1.16430	0.82820
3	C	-1.29040	-1.16430	0.57860
4	C	0.14410	-1.16430	-1.40680
5	C	-2.31570	-1.97870	0.06380
6	C	-1.61740	-0.30290	1.65140
7	C	-0.62150	-0.30290	-2.22640
8	C	2.23890	-0.30290	0.57500
9	C	1.10260	-1.97870	-2.03740
10	C	1.21310	-1.97870	1.97360
11	C	-3.90170	-1.16430	1.67460
12	C	3.40100	-1.16430	2.54170
13	C	0.50060	-1.16430	-4.21620
14	C	-3.59060	-1.97870	0.56530
15	C	-0.47930	-0.30290	-3.59280
16	C	1.30570	-1.97870	-3.39220
17	C	3.35110	-0.30290	1.38130
18	C	2.28490	-1.97870	2.82690
19	C	-2.87180	-0.30290	2.21150
20	C	14.0756	0.99150	7.51610
21	C	-13.5470	0.99150	8.43170
22	C	-0.52860	0.99150	-15.9479
23	C	14.8075	1.97870	6.66850
24	C	-13.1789	1.97870	9.48940
25	C	-1.62860	1.97870	-16.1580

26	C	-11.4100	1.16430	7.61360
27	C	-0.88860	1.16430	-13.6881
28	C	12.2985	1.16430	6.07450
29	C	-9.65210	-0.55000	4.63510
30	C	8.84010	-0.55000	6.04150
31	C	0.81200	-0.55000	-10.6765
32	C	-14.8756	0.55000	8.37690
33	C	14.6924	0.55000	8.69420
34	C	0.18320	0.55000	-17.0711
35	C	-10.3847	0.67290	6.66320
36	C	-0.57810	0.67290	-12.3250
37	C	10.9628	0.67290	5.66180
38	C	-1.89710	2.33220	-17.4807
39	C	-14.1902	2.33220	10.3833
40	C	16.0873	2.33220	7.09740
41	N	-12.6648	0.55000	7.48380
42	N	12.8135	0.55000	7.22620
43	N	-0.14870	0.55000	-14.7099
44	C	-11.0789	1.97870	8.65070
45	C	-1.95230	1.97870	-13.9199
46	C	13.0311	1.97870	5.26930
47	C	0.40990	-0.06940	-11.9769
48	C	10.1674	-0.06940	6.34350
49	C	-10.5773	-0.06940	5.63350
50	C	0.99060	-1.16430	-8.20960
51	C	6.61450	-1.16430	4.96270
52	C	-7.60510	-1.16430	3.24690
53	C	16.6687	1.82600	8.21900
54	C	-1.21650	1.82600	-18.5450

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55	C	-15.4522	1.82600	10.3260
56	C	-9.86690	-1.51910	3.62310
57	C	8.07120	-1.51910	6.73340
58	C	1.79570	-1.51910	-10.3566
59	C	15.9688	0.99150	9.02470
60	C	-15.8000	0.99150	9.31710
61	C	-0.16880	0.99150	-18.3417
62	N	14.2443	2.33220	5.53750
63	N	-11.9178	2.33220	9.56720
64	N	-2.32650	2.33220	-15.1047
65	C	-8.75150	-1.97870	2.82280
66	C	6.82040	-1.97870	6.16760
67	C	1.93110	-1.97870	-8.99040
68	C	4.52590	-1.16430	3.38830
69	C	-5.19730	-1.16430	2.22540
70	C	0.67140	-1.16430	-5.61370
71	S	-0.07870	-0.19630	-9.21040
72	S	-7.93710	-0.19630	4.67340
73	S	8.01580	-0.19630	4.53700
74	C	0.82680	-1.16430	-6.82680
75	C	5.49880	-1.16430	4.12940
76	C	-6.32560	-1.16430	2.69740
77	H	-2.08550	-2.74860	-0.80490
78	H	0.34570	-2.74860	2.20850
79	H	2.22150	0.41640	-0.30990
80	H	-0.84230	0.41640	2.07880
81	H	1.73980	-2.74860	-1.40370
82	H	-1.37910	0.41640	-1.76890
83	H	-3.09410	0.55000	3.05030

84	H	4.18870	0.55000	1.15440
85	H	2.29760	-2.74860	3.70390
86	H	-1.09460	0.55000	-4.20480
87	H	-4.35650	-2.74860	0.13780
88	H	2.05890	-2.74860	-3.84180
89	H	-13.8896	3.02300	11.1677
90	H	-2.72670	3.02300	-17.6126
91	H	16.6163	3.02300	6.44490
92	H	-15.1298	-0.06940	7.58690
93	H	14.1353	-0.06940	9.30930
94	H	0.99450	-0.06940	-16.8962
95	H	10.6099	1.16430	4.73030
96	H	-9.40150	1.16430	6.82330
97	H	-1.20840	1.16430	-11.5536
98	H	1.00810	-0.55000	-12.7830
99	H	10.5664	-0.55000	7.26450
100	H	-11.5745	-0.55000	5.51850
101	H	-10.0638	2.33220	8.71590
102	H	12.5801	2.33220	4.35760
103	H	-2.51630	2.33220	-13.0735
104	H	16.4286	0.55000	9.93750
105	H	-16.8204	0.55000	9.25890
106	H	0.39180	0.55000	-19.1963
107	H	2.42420	-1.97870	-11.1247
108	H	-10.8464	-1.97870	3.46300
109	H	8.42220	-1.97870	7.66170
110	H	-16.2005	2.13890	11.0510
111	H	-1.47020	2.13890	-19.5555
112	H	17.6707	2.13890	8.50460

113	H	6.08000	-2.33220	6.59280
114	H	-8.74950	-2.33220	1.96900
115	H	2.66950	-2.33220	-8.56180

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Chromophore 5

Total energy = -7.328964419E+4 eV, -2.693412672E+3 hartree, -1.690124532E+6 kcal/mol

Cartesian coordinates

N	Atom	X	Y	Z
1	N	0.0000	-0.03060	0.0000
2	C	1.31150	-0.03060	-0.52470
3	C	-0.20140	-0.03060	1.39820
4	C	-1.11020	-0.03060	-0.87350
5	C	-2.21880	-0.82590	-0.60740
6	C	-1.12670	0.82590	-2.01600
7	C	0.58340	-0.82590	2.22520
8	C	-1.18250	0.82590	1.98370
9	C	1.63540	-0.82590	-1.61790
10	C	2.30920	0.82590	0.03230
11	C	-3.33160	-0.03060	-2.62860
12	C	3.94230	-0.03060	-1.57090
13	C	-0.61070	-0.03060	4.19960
14	C	0.38190	-0.82590	3.60330
15	C	-1.38880	0.82590	3.35800
16	C	2.92960	-0.82590	-2.13240
17	C	3.60250	0.82590	-0.47620
18	C	-3.31150	-0.82590	-1.47090
19	C	-2.21370	0.82590	-2.88180
20	C	-8.71950	-0.15760	-6.92620
21	C	-1.63860	-0.15760	11.0144
22	C	10.3580	-0.15760	-4.08820
23	C	-6.48920	-0.03060	-5.14690
24	C	7.70190	-0.03060	-3.04640
25	C	-1.21270	-0.03060	8.19330

26	C	10.0315	0.61370	-2.95710
27	C	9.32020	-0.82590	-4.71350
28	C	-2.45480	0.61370	10.1661
29	C	-0.57810	-0.82590	10.4283
30	C	-8.74210	-0.82590	-5.71480
31	C	-7.57670	0.61370	-7.20900
32	C	-6.49790	0.61370	-6.34610
33	C	-7.64220	-0.82590	-4.85600
34	C	-2.24690	0.61370	8.80040
35	C	8.74480	0.61370	-2.45430
36	C	8.02650	-0.82590	-4.19030
37	C	-0.38430	-0.82590	9.04630
38	C	-1.80770	-0.15760	12.4550
39	C	11.6902	-0.15760	-4.66200
40	C	-9.88250	-0.15760	-7.79300
41	C	5.25440	-0.03060	-2.08660
42	C	-4.43430	-0.03060	-3.50710
43	C	-0.82010	-0.03060	5.59380
44	C	-10.0685	0.15760	-8.98780
45	C	12.8180	0.15760	-4.22570
46	C	-2.74940	0.15760	13.2135
47	C	-0.99890	-0.03060	6.80560
48	C	6.39330	-0.03060	-2.53770
49	C	-5.39430	-0.03060	-4.26790
50	C	-2.91180	0.15760	14.6568
51	C	-11.2373	0.15760	-9.85010
52	C	14.1491	0.15760	-4.80680
53	H	1.33080	-1.56860	1.82450
54	H	-0.28740	1.56860	-2.23380

55	H	-2.24540	-1.56860	0.24030
56	H	0.91460	-1.56860	-2.06470
57	H	-1.79080	1.56860	1.36580
58	H	2.07820	1.56860	0.86800
59	H	4.36250	1.56860	-0.03310
60	H	0.97560	-1.56860	4.24860
61	H	-2.15260	1.56860	3.79460
62	H	-4.16720	-1.56860	-1.27940
63	H	-2.20990	1.56860	-3.76150
64	H	3.19160	-1.56860	-2.96920
65	C	-12.4094	-0.48160	-9.54320
66	C	14.4693	-0.48160	-5.97520
67	C	-2.05990	-0.48160	15.5184
68	N	15.1208	0.82590	-4.15480
69	N	-11.1586	0.82590	-11.0175
70	N	-3.96220	0.82590	15.1724
71	C	-4.13990	0.82590	16.4878
72	C	-12.2089	0.82590	-11.8292
73	C	16.3488	0.82590	-4.65860
74	H	9.52820	-1.56860	-5.55880
75	H	10.7960	1.20510	-2.46030
76	H	0.04990	-1.56860	11.0310
77	H	-7.52870	1.20510	-8.11950
78	H	-9.57810	-1.56860	-5.47230
79	H	-3.26730	1.20510	10.5797
80	H	0.41440	-1.56860	8.61730
81	H	-2.87820	1.28010	8.17200
82	H	7.25560	-1.56860	-4.66750
83	H	-7.67000	-1.56860	-3.94980

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84	H	-5.63800	1.28010	-6.57860
85	H	8.51630	1.28010	-1.59340
86	C	16.6442	0.03060	-5.80930
87	C	-3.29110	0.03060	17.3189
88	C	-13.3531	0.03060	-11.5097
89	H	11.7667	-0.82590	-5.53900
90	H	-10.6803	-0.82590	-7.42080
91	H	-1.08640	-0.82590	12.9598
92	N	-13.4291	-0.61370	-10.5050
93	N	15.8121	-0.61370	-6.37740
94	N	-2.38300	-0.61370	16.8824
95	H	-9.29190	0.93990	-9.40580
96	H	12.7916	0.93990	-3.34410
97	H	-3.49970	0.93990	12.7499
98	H	-1.19920	-0.93990	15.1336
99	H	-12.5064	-0.93990	-8.60530
100	H	13.7057	-0.93990	-6.52820
101	H	-4.99110	1.56860	16.8960
102	H	17.1279	1.56860	-4.12560
103	H	-12.1369	1.56860	-12.7704
104	H	17.6566	0.03060	-6.20640
105	H	-3.45340	0.03060	18.3943
106	H	-14.2032	0.03060	-12.1879

ACCEPTED MANUSCRIPT