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Strong solvent dependence of linear and non-linear optical properties of donor-acceptor type pyrrolo[3,2-*b*]pyrroles

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We describe the design, synthesis, and fluorescent profile of two environment-sensitive dyes in which an electron-donating group is conjugated to an electron-accepting unit *via* a pyrrolo[3,2-*b*]pyrrole ring system. The maximum emission wavelength (λ_{em}) of these donor-donor-acceptor (D-D-A) pyrrolo[3,2-*b*]pyrroles was found to be very sensitive to the environment (bathochromic shift of about 100 nm in polar solvents). The longer emission wavelength in polar aprotic as well as hydrophilic solvents compared with that in a low-polarity hydrophobic solvents was due to an ICT character of the excited state. The Stokes shift increased in both cases following the polarity differences, reaching ~7000 cm^{-1} in MeOH for the compound possessing a cyano group and dimethylamino groups at the periphery. Interestingly, the two-photon absorption responses were also found to be quite sensitive to solvent polarity with an increase by a factor of about 2 on going from apolar solvent to highly polar protic or aprotic solvent.

Introduction:

The relationship between the structure of organic compounds and their linear and non-linear optical properties has fascinated scientists from a variety of vantage points.[1,2] The understanding of this relationship becomes even more important in light of recent interest in functional dyes, particularly their use in organic field-effect transistors,[3] organic light-emitting diodes,[4] and organic photovoltaics.[5]

1,4-Dihydropyrrolo[3,2-*b*]pyrroles, although known since 1972, were not intensely investigated until 2013 when a one-pot synthesis of these compounds was developed.[6] The combined effect of desirable optical properties and straightforward synthesis made it possible to quickly expand this area of research in different directions.[7] Inherently high fluorescence quantum yields of pyrrolo[3,2-*b*]pyrroles and promising values of two-photon absorption (2PA) cross-sections[7b,8] inclined us to use them as models to study the influence of polarity on their optical properties. Such studies are usually performed on dipolar compounds possessing carbon-carbon double bonds (which inevitably leads to Z/E isomers) or carbon-carbon triple bonds (which allow for full overlap of orbitals of all moieties in one conformation only).[9] Fully rigid donor-acceptor (D-A) dyes such as acedan have also been studied.[10] For dyes possessing biaryl linkages, the optical response depends on the actual width of the dihedral angles. Interestingly, D-A dyes built from a oligothiophene π-conjugated systems have been shown to lead to a sizeable 2PA response as well as good fluorescence quantum yield leading to large 2P brightnesss,[11] demonstrating the potential of extended heteroaromatics systems as favorable moieties for increased 2P brigthness of push-pull systems. Previous studies[7,8] suggested that, pyrrolo[3,2-*b*]pyrroles have relatively small mean dihedral angles between substituents at positions 2 and 5 and the core, an advantage which ensures partial conjugation of the entire chromophore. We therefore undertook an investigation to determine how this exceptionally rich π-linker will influence communication between the electron-donating and electron-withdrawing groups located at the periphery of the molecule.

Results and discussion:

Design and synthesis

Since the methodology leading to tetraaryl-pyrrolo[3,2-*b*]pyrroles (TAPPs) inevitably produces compounds possessing C_2 symmetry,[6,7b] in order to prepare desired donor-acceptor type compounds we attempted to resolve to the statistical synthesis. We chose methoxy and dialkylamino groups as donors and the cyano group as the electron-acceptor. Given that yields of TAPPs can reach 50%[7b,c] we had reasonable expectations that statistical condensations of 4-cyanobenzaldehyde (**1**) and 4-methoxybenzaldehyde (**2**) with

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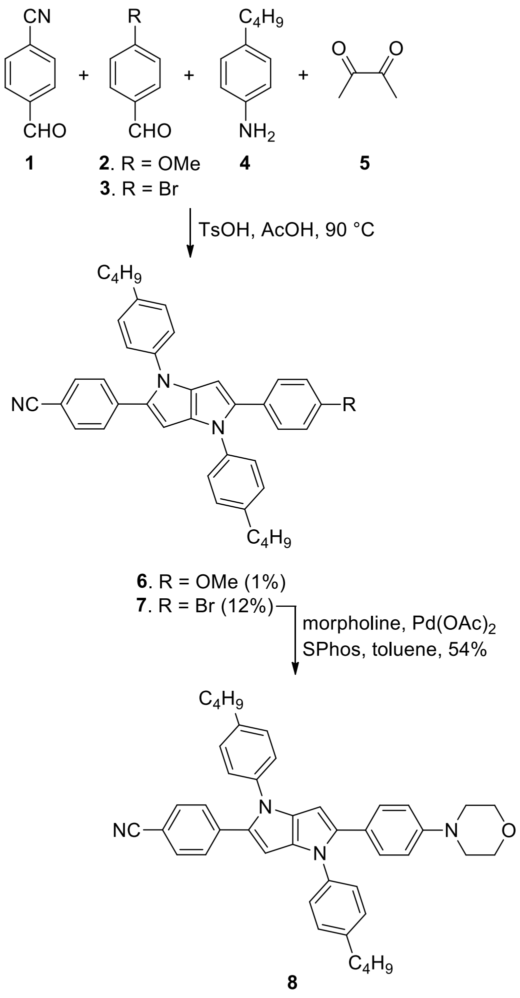
† Electronic Supplementary Information (ESI) available: Copies of ^{1}H NMR and ^{13}C NMR spectra for compounds **6**, **7** and **8** as well as selected optical and computational data. See DOI: 10.1039/x0xx00000x

4-*n*-butylaniline (**4**) and diacetyl (**5**) can give reasonable quantities of TAPPs bearing two different substituents at positions 2 and 5. However, the corresponding TAPPs **6** was obtained in 1% yield (Scheme 1). Poor yield in the first case can be rationalized by the intrinsically lower reactivity of the electron-rich 4-methoxybenzaldehyde (**2**), making the distribution of products fall far from statistically predicted values. The analogous condensation of 4-morpholinobenzaldehyde with 4-cyanobenzaldehyde and 4-*n*-butylaniline did not lead to the formation of any mix-condensation product. Therefore, we turned to another strategy leading to the corresponding pyrrolo[3,2-*b*]pyrrole **8**. Condensation involving 4-bromobenzaldehyde (**3**) and 4-cyanobenzaldehyde (**1**) afforded TAPP **7** in 12% yield (Scheme 1). Subsequently, Buchwald-Hartwig reaction[12] of TAPP **7** with morpholine afforded tertiary amine **8** in 51% yield (Scheme 1).



Scheme 1. Synthesis of TAPPs **6**-**8**.

Optical studies

Optical properties of TAPPs **6** and **8** were studied in six solvents spanning the polarity scale (Table 1, Figs. 1-3). We aimed to probe the magnitude of interaction of the two parts of the molecule through the electron-rich pyrrolo[3,2-*b*]pyrrole linker. According to predictions, by enhancing the donor strength (**6**→**8**), a red-shift of the λ_{abs} by approximately 5-10 nm can be achieved. In addition, we also observed a slight hyperchromic shift.

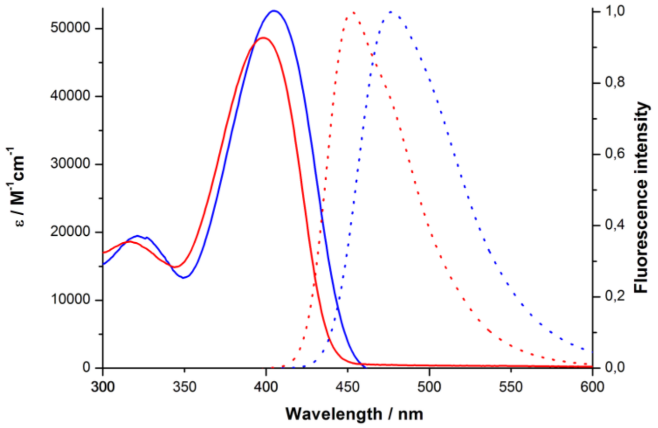


Fig. 1 Absorption (solid) and emission (dotted) spectra of compounds **6** (red line) and **8** (blue line) measured in toluene.

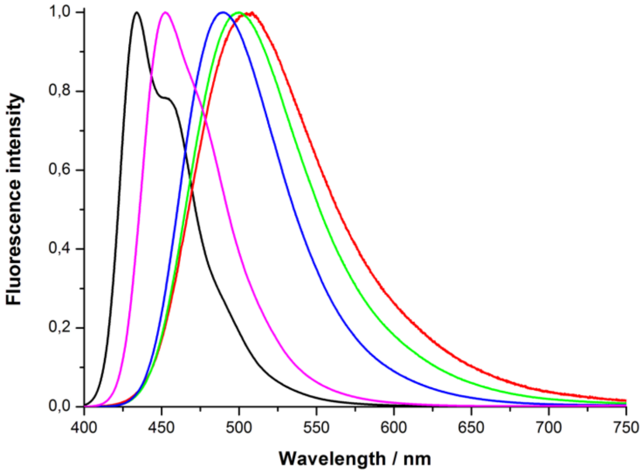


Fig. 2 Fluorescence spectra of compounds **6** measured in cyclohexane (black line), toluene (magenta line), dichloromethane (blue line), acetonitrile (green line) and methanol (red line).

Table 1. Spectroscopic optical properties of compounds **6** and **8**.

Cpd	Solvent	λ_{abs} [nm]	λ_{em} [nm]	Stokes Shift [10^3 cm^{-1}]	Φ_{fl}	τ ns	$2\lambda_{OPA}$ [nm]	λ_{TPA}^{max1} [nm]	$\sigma_2^{max1}\Phi$ [GM]	σ_2^{max1} [GM]
6	Cyclohexane	399	434	2.0	0.87[a] 0.94[b]	1.5	798	810 770	110 96	112 98
	Toluene	399	453	3.0	0.84[a] 0.89[b]	1.6	798	820	120	120
	CH_2Cl_2	398	491	4.8	0.86[a] 0.78[b]	2.3	796	820	120	148
	CH_3CN	391	504	5.7	0.45[a] 0.41[b] 0.46[c]	1.8	782	800	55	120
	MeOH	396	503	5.4	0.05[a] 0.065[c]	0.2 (92%) 2.5 (8%)	792	820 790	13 17	200 260
	DMSO	399	505	5.3	0.71[a] 0.73[b]	2.1	798	820	160	222
8	Cyclohexane	403	452	2.7	0.83[a] 0.85[b]	1.5	805	820	170	179
	Toluene	406	478	3.7	0.82[a] 0.85[b]	1.5	812	820	180	184
	CH_2Cl_2	405	529	5.8	0.70[a] 0.79[b] 0.83[c]	2.2	810	820	120	145
	CH_3CN	397	554	7.1	0.22[a] 0.20[b] 0.22[c]	0.8	794	820	50	227
	MeOH	401	554	6.9	0.03[a,b] 0.035[c]	0.13 (98%) 3.1 (2%)	802	830 770	11 7	314 200
	DMSO	408	571	7.0	0.44[a] 0.43[b]	1.4	816	830	140	340

[a] Standard: Fluorescein in NaOH 0.01M (Φ=0.9) [b] Standard: Rhodamine 6G in EtOH (Φ=0.94). [c] Determined with perylene in cyclohexane as a standard.

The absorption maxima of both **6** and **8** were found to be only weakly sensitive to polarity differences (with variation of the maximum absorption wavelength not larger than 10 nm), which is presumably related to changes in dipole moments in the ground state. On the other hand, both compounds displayed strong positive solvatochromism of fluorescence. With increased solvent polarity, the emission spectra of both compounds broaden and exhibit a significant red shift. This is attributed to a highly polarized ICT excited state, which is typical for D–π–A compounds.[13] From cyclohexane to MeOH, the emission maxima (λ_{em}) of **6** shifted from 434 to 503 nm and the color of the emission varied from blue to green. Fluorescence quantum yields of products **6** and **8** were very high in non-polar solvents. In the case of compound **8**, the maximum of emission moved bathochromically from 452 nm in cyclohexane to 554 in MeOH (Table 1, Fig. 3). The fluorescence quantum yields of TAPPs **6** and **8** decrease in polar solvents as a result of the bathochromic shift of the emission band which induced both a reduction of the radiative decay rate (as predicted by the Strickler-Berg equation)[14] and an increase in the non-radiative decay rate. DMSO led to larger fluorescence quantum yield as compared to CH_3CN, as expected from its much higher viscosity which slowed vibrational decay (Table 1). We observed that a protic polar solvent like methanol led to much lower fluorescence quantum yields as well as shorter fluorescence lifetimes. This effect originated from effective non-radiative decay processes which overcame radiative decay (see Table 1) and can be ascribed to the formation of H-bonds between MeOH and the CN end-groups in both TAPPs derivatives, thus providing efficient vibrational decay channels.

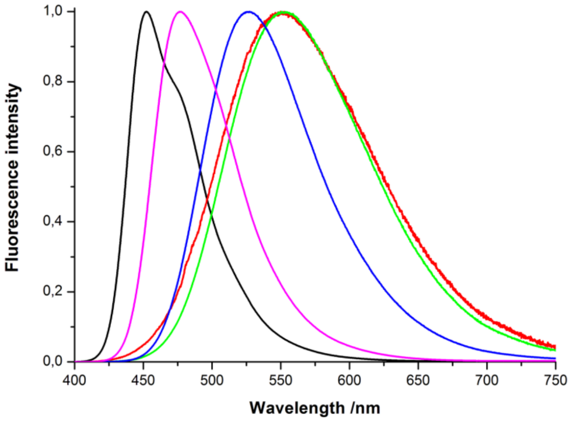


Fig. 3 Fluorescence spectra of compounds **8** measured in cyclohexane (black line), toluene (magenta line), dichloromethane (blue line), acetonitrile (green line) and methanol (red line).

We observed that Stokes shift values were always larger for compound **8** compared to compound **6**, revealing a more pronounced intramolecular charge redistribution and subsequent nuclear reorganization upon excitation (Table 1). This difference could be explained by ICT,[15] and may be more precisely related to the presence of a stronger electron-donating end-group in molecule **8** (i.e., morpholine moiety instead of methoxy). This stronger electron-donating moiety is also responsible for the bathochromic and hyperchromic shifts of both absorption and emission bands of **8** as compared to **6**. The analysis of the solvatochromic behavior provided further insight into the difference in ICT amplitude for the two molecules. The Stokes shift values displayed a linear dependence on the polarity-polarizability function Δf for both compounds following the Lippert-Mataga correlation[16] (Equation 1):

$$\nu_{abs} - \nu_{em} = 2\Delta\mu^2\Delta f/(hca^3) + \mathrm{const}(1)$$

where ν_{abs} (ν_{em}) is the wavenumber of the absorption (fluorescence) maximum, $\Delta\mu$ is the change of dipole moment between the ground state and the emitting state, *h* is the Planck constant, *c* is the light velocity, *a* is the radius of the Onsager spherical cavity, and $\Delta f = (\varepsilon - 1)/(2\varepsilon + 1) - (n^2 - 1)/(2n^2 + 1)$, where ε is the dielectric constant and *n* the refractive index of the solvent.

The slope values derived from the Lippert-Mataga linear correlations (see Figure S1 and S2) were 10 300 and 13 100 cm^{-1} for molecules **6** and **8**, respectively. These specific shift values which quantify the sensitivity to solvent polarity were notable, although not as large as reported polarity D-π-A probes.[17] Specific shift values are directly related to $\Delta\mu^2/a^3$. Since both compounds were of similar size (and thus had similar Onsager cavity radii), the larger specific solvatochromic shift determined in the case of compound **8** indicated indeed a larger $\Delta\mu$ value and therefore more pronounced photo-induced ICT for the TAPP derivative bearing the stronger electron-donating end-group.

To gain deeper insight into the ICT amplitude in the two molecules, the electronic structures of both the ground state and first optically allowed excited state were determined by means of DFT calculations. Table 2 reports the calculated spectroscopic properties of compounds **6** and **8**, together with the electric dipoles of the ground (μ_g) and excited state (μ_e), as well as their difference $\Delta\mu = |\overrightarrow{\mu_e} - \overrightarrow{\mu_g}|$. From the analysis of the total electron densities of the two electronic states, $\Delta\mu$ is further decomposed as $\Delta\mu = q^{CT} \times d^{CT}$, where q^{CT} is the photo-induced charge transfer, *i.e.* the global amount of charge transferred upon light excitation, and d^{CT} is the distance over which this charge is transferred.[18] The calculations were conducted in the two solvents that display the largest difference in their static dielectric constant, namely cyclohexane (ε_0 = 2.0165) and DMSO (ε_0 = 46.826).

Consistent with the experimental findings, the maximal absorption wavelengths of the two compounds are little impacted by the solvent polarity, although the calculated red shift when going from cyclohexane to DMSO is slightly more pronounced (15 nm) than that measured (0-5 nm). Enhancing the donor strength by replacing the methoxy by a morpholine substituent (**6**→**8**) induces a redshift of the λ_{abs} of 4-5 nm. The slight hyperchromic shift observed experimentally is also well reproduced by the DFT calculations, as indicated by the increase of the oscillator strengths from compound **6** to compound **8**. As expected for π-conjugated dyes, the lowest-energy absorption band is mainly associated to an electronic transition from the highest occupied molecular orbital (HOMO) to the lowest occupied one (LUMO). The shapes of these two frontier MOs (see Figure 4 for compound **8**) further reveal a significant ICT from the donor moiety to the acceptor one, which is illustrated equivalently by the electron density difference between the ground and the lowest-energy excited state (Figure 5). This charge transfer occurring throughout the molecules upon light irradiation can be quantified by the dipole moment variation $\Delta\mu$ between the two involved electronic states. In both solvents, $\Delta\mu$ is slightly larger for compound **8** than for compound **6**, which confirms the assumption that the larger Stokes' shift values observed for compound **8** originate from a more pronounced intramolecular charge redistribution preceding the nuclear relaxation. Further analysis of the electron densities of the ground and excited states indicates that the increase of $\Delta\mu$ from **6** to **8** is due to a slight enhancement of the charge transfer distance d^{CT}, the total charge transferred q^{CT} being of the same magnitude in the two derivatives.

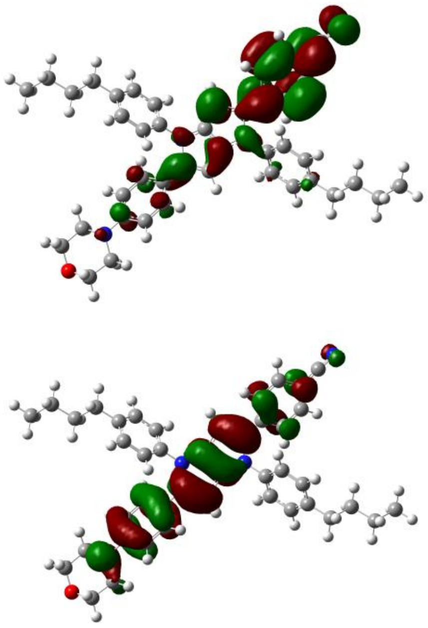


Fig. 4 HOMO (bottom) and LUMO (top) of compound **8**, as calculated at the TDDFT/M06-2X/6-311G(d) level in DMSO.

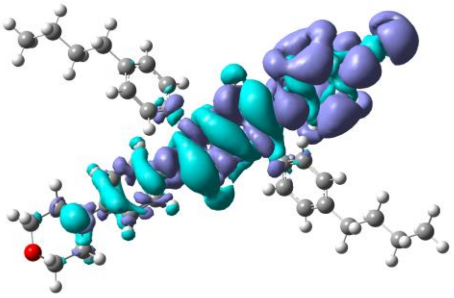


Fig. 5 Electron density difference between the lowest-energy excited state and the ground state for compound **8**, Δρ = ρ(excited) − ρ(ground), as calculated at the TDDFT/M06-2X/6-311G(d) level in DMSO. Dark (light) blue lobes are associated with positive (negative) Δρ values.

Table 2. Maximal absorption wavelength (λ_{abs}, nm), transition energy (ΔE_{abs}, eV), oscillator strength (f), ground state and excited state dipole moments (μ_g and μ_e, D), dipole moment variation ($\Delta\mu = |\vec{\mu_e} - \vec{\mu_g}|$, D), charge transferred upon excitation (q^{CT}, |e|) and charge transfer distance (d^{CT}, Å) calculated for compounds **6** and **8** in cyclohexane and DMSO at the TDDFT/M06-2X/6-311G(d) level.

cpd	solvent	λ_{abs}	ΔE_{abs}	*f*	μ_g	μ_e	q^{CT}	d^{CT}	$\Delta\mu$
6	cyclohexane	358	3.459	1.42	7.62	17.91	0.66	3.24	10.3
	DMSO	374	3.318	1.69	8.33	20.73	0.68	3.81	12.4
8	cyclohexane	363	3.417	1.56	7.11	17.55	0.66	3.32	10.5
	DMSO	378	3.284	1.80	7.97	20.91	0.68	3.97	13.0

Thanks to their strong fluorescence, the 2PA response of compounds **6** and **8** could be experimentally investigated in various solvents using the two-photon induced fluorescence (TPEF) technique developed by Webb and collaborators.[19] Two-photon absorption responses are known to be sensitive to various local electrostatic effects including environmental effects.[20] In particular, the environmental effects encompass the effect of solvation of a dipolar push-pull chromophore.[21] Frequently, 2PA responses decrease in polar solvents such as water or MeOH.[22] One of the aims of the current project was to investigate the two-photon absorption cross-section of these D-D-A systems and to study the dependence of 2PA on solvent parameters. The 2PA cross-sections (σ_2) were thus measured in cyclohexane, toluene, CH_2Cl_2, acetonitrile, DMSO and methanol (Table 1, Figure 6). In contrast to previously studied centrosymmetric TAPPs,[7b,8] the current dipolar compounds **6** and **8** displayed the lowest excited states allowed for both one and two-photon absorbance and the 2PA band was observed at twice the wavelength corresponding to the maximum one-photon absorption (Table 1, ESI). We found that in both cases and for all solvents the maxima of two-photon absorption were located at 770-830 nm. Compound **8** showed larger 2PA responses than compound **6** (Table 1). The 2PA responses vary from 100 GM to 260 GM depending on the environment in the case of compound **6** and from 145 to 340 GM in the case of compound **8** (Figure 6). Interestingly, we observed that the nature of the environment strongly influenced the 2PA response of both compounds. Whereas the position of the 2PA maximum was not much affected (as was the case for one-photon absorption), the amplitude of the band was found to vary markedly with the nature and polarity of the solvent. Indeed, the peak 2PA responses of compounds **6** and **8** were found to almost double on going from apolar cyclohexane to polar DMSO. This marked increase could be ascribed to the effect of the solvent reaction field created by the dipolar chromophores. [20]

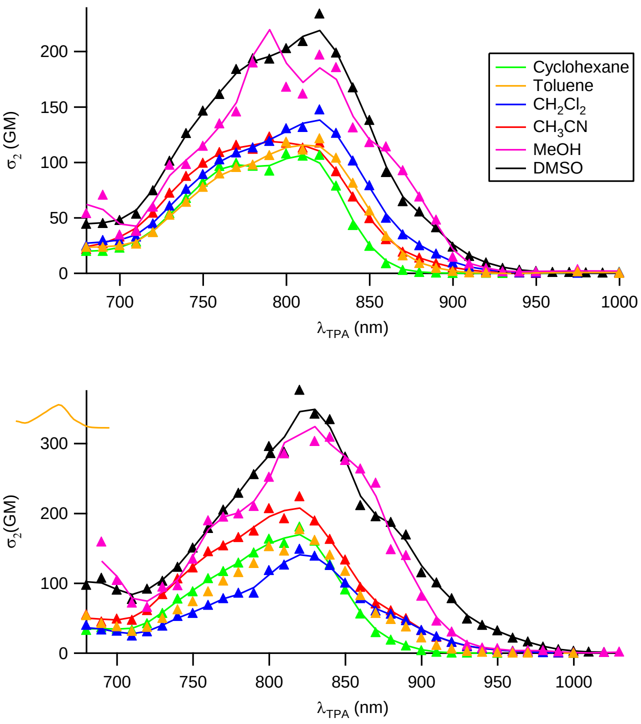


Fig. 6 Two-photon absorption spectra of compounds **6** (top) and (bottom) **8** measured in solvents of various polarity.

As the fluorescence quantum yield decreased with increased polarity, the 2P brightness increased by about 50% in the case of compound **6** in DMSO (160 GM). In contrast, the 2P brightness of compound **8** was the highest in apolar toluene (180 GM) due to the much steeper decrease of fluorescence quantum yield with increased polarity in the case of compound **8**.

A remarkable effect was observed in the case of methanol which produced a major increase in the peak 2PA response. Indeed an increase of about 130% was noted for compound **6** and by about 75% for dye **8**. This marked increase can be ascribed to the H-bond between the proton of MeOH and the cyano electron-withdrawing (EW) group. This H-bond induces an increase of polarization and consequently an increase of the 2PA response of compounds **6** and **8**.[21] As this H-bond was also responsible for efficient vibrational decay; this did not however lead to an increase in brightness and actually the 2P brightness was the lowest in MeOH (and basically one-order of magnitude smaller than in DMSO).

Conclusions

The pyrrolo[3,2-*b*]pyrrole core was determined to be an efficient linker allowing conjugation of peripheral benzene rings. The resulting dipolar compounds displayed strong solvatochromism of fluorescence and moderately strong S_1-S_0 transitions leading to compounds possessing two-photon absorption cross-section values of ~200-400 GM at ~750 nm. Interestingly, the 2PA responses were found to increase by about a factor of two on going from a apolar solvent to a highly polar aprotic or protic solvent. The emission was almost quantitative in toluene and cyclohexane but decreased dramatically in a protic solvent such as methanol, most probably in relation with H-bonding between protic solvent and the cyano end-group of TAPPs derivative. Slowing the vibrational decay due to the higher viscosity is responsible for to larger fluorescence quantum yield DMSO led as compared to CH_3CN. Experimental observations are in full agreement with DFT calculations revealing significant intramolecular charge transfer from the donor moiety to the acceptor one. Functional dyes of this type can find use in hydrophobic sensors in stimulus-responsive macromolecules such as synthetic polymers and proteins.[23]

Experimental Section

General methods

All chemicals and solvents were reagent grade and used without purification, unless otherwise noted. Toluene and morpholine were dried according to the standard procedures.[24] Moisture sensitive reactions were performed under an argon atmosphere using flame-dried glassware. Thin-layer chromatography (TLC, silica gel 60 F254) was used to monitor the reaction progress. Product purifications were performed by means of dry column vacuum chromatography (DCVC) with silica gel Type D 5F. Melting points were determined by using a capillary-type automated melting point apparatus. The identity of all compounds was established using ^1H and ^{13}C NMR (measured on Varian 500MHz) and HRMS (ES). Chemical shifts (δ) are given in parts per million (ppm) relative to TMS Coupling constants (*J* values) are given in Hertz (Hz).

General procedure for the synthesis of pyrrolo[3,2-*b*]pyrroles 6 and 7

Glacial acetic acid (2ml) was placed in a two-necked 25 ml flask equipped with a reflux condenser, followed by the addiction of aryl amine (2 mmol), corresponding two aldehydes (1 mmol each), and TsOH (0.2 mmol). The resulting solution was stirred for 30 minutes at 90°C. Subsequently butane-2,3-dione (1 mmol) was added dropwise via syringe, and the solution was stirred for 3 h at 90 °C. The reaction mixture was cooled to room temperature and the precipitate was filtered and washed with cooled glacial acetic acid. The purification of each compound is described as follows.

1,4-Bis(4-butylphenyl)-2-(4-methoxyphenyl)-5-(4-cyanophenyl)-1,4-dihydropyrrolo[3,2-*b*]pyrrole (**6**). Following the general procedure, amine **4** and aldehydes **1** and **2** were reacted. The obtained precipitate was purified by means of DCVC (silica, toluene/hexanes 50:50, then toluene) and crystallized from CH_2Cl_2/cyclohexane giving yellow solid **6**. Yield: 12 mg (1 %). R_f=0.26 (SiO_2; toluene/hexanes, 1:1). M.p. 203–204 °C. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.43 (d, *J*=8.5 Hz, 2H, H_{arom}), 7.25 (d, *J*=6.5 Hz, 2H, H_{arom}), 7.21-7.13 (m, 10H, H_{arom}), 6.77 (d, J=8.5 Hz, 2H, H_{arom}), 6.49 (s, 1H, H_{arom}), 6.29 (bs, 1H, H_{arom}), 3.78 (s, 3H, CH_3), 2.67-2.61 (m, 4H, $2CH_2$), 1.67-1.59 (m, 4H, $2CH_2$), 1.41-1.36 (m, 4H, $2CH_2$), 0.97-0.93 ppm (m, 6H, $2CH_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.4, 141.1, 140.6, 138.2, 137.6, 137.4, 137.3, 133.6, 132.9, 131.8, 131.2, 129.6, 129.3, 129.3, 129.0, 127.5, 126.0, 125.1, 125.1, 119.4, 113.6, 96.5, 93.3, 55.2, 35.2, 33.5 (2 signals), 22.4, 14.0 (2 signals) ppm. HRMS (ES): m/z: calcd for $C_{40}H_{39}N_3O$: 577.3093 $[M^{\cdot}]^+$; found: 577.3091.

1,4-Bis(4-butylphenyl)-2-(4-bromophenyl)-5-(4-cyanophenyl)-1,4-dihydropyrrolo[3,2-*b*]pyrrole (**7**). Following the general procedure, amine **4** and aldehydes **1** and **3** were reacted. Obtained precipitate was purified by means of DCVC (silica, toluene/hexane 25:75, then toluene) and crystallized from CH_2Cl_2/cyclohexane giving yellow solid **7**. Yield: 150 mg (12 %). R_f=0.35 (SiO_2; toluene/hexanes, 1:1). M.p. 246–24 7°C. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.45 (d, *J*=8.5 Hz, 2H, H_{arom}), 7.33 (d, *J*=8.5 Hz, 2H, H_{arom}), 7.26 (d, *J*=8.5 Hz, 2H, H_{arom}), 7.21-7.14 (m, 8H, H_{arom}), 7.07 (d, *J*=8.5 Hz, 2H, H_{arom}), 6.48 (s, 1H, H_{arom}), 6.35 (s, 1H, H_{arom}), 2.67-2.62 (m, 4H, $2CH_2$), 1.67-1.60 (m, 4H, $2CH_2$), 1.43-1.35 (m, 4H, $2CH_2$), 0.96 ppm (t, *J*=7.3 Hz, 6H, $2CH_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.3, 141.1, 138.0, 137.1, 136.1, 133.8, 133.5, 132.3, 131.9, 131.3, 129.5, 129.2, 127.6, 125.2, 125.1, 120.4, 119.3, 108.6, 96.2, 94.4, 35.2, 33.5, 22.4 (2 signals), 14.0 ppm. HRMS (ES): m/z: calcd for $C_{39}H_{36}N_3Br$: 625.2093 $[M^{\cdot}]^+$; found: 625.2089.

1,4-Bis(4-butylphenyl)-2-(4-morpholinephenyl)-5-(4-cyanophenyl)-1,4-dihydropyrrolo[3,2-*b*]pyrrole (**8**). A 20 ml flame dried Schlenk flask containing **7** (98.4 mg, 0.15 mmol), palladium(II) acetate (1.1 mg, 0.005 mmol), 2-dicyclohexylphosphino-2’,6’-dimethoxybiphenyl (6.2 mg, 0.015 mol), and cesium carbonate (147 mg, 0.45 mmol) was evacuated and backfilled with argon 3 times. Four ml of anhydrous toluene and morpholine (20 µl, 0.23 mmol) were added. The Schlenck flask was again evacuated and backfilled with argon (3 times), closed firmly and the solution was stirred overnight at 120 °C. After cooling, CH_2Cl_2 and water were added, layers separated and aqueous layer extracted with dichloromethane 5 times. Combined organic layers were washed twice with water and dried over Na_2SO_4. Evaporation and purification by means of DCVC (silica, ethyl acetate/hexane 20:70) and crystallization from CH_2Cl_2/cyclohexane gave yellow solid **8**. Yield: 50 mg (51 %). R_f=0.62 (SiO_2; toluene). M.p. 204–205 °C. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.43 (d, *J*=8 Hz, 2H, H_{arom}), 7.25 (d, *J*=10 Hz, 2H, H_{arom}), 7.21-7.13 (m, 10H, H_{arom}), 6.79 (bs, 2H, H_{arom}), 6.49 (s, 1H, H_{arom}), 6.27 (s, 1H, H_{arom}), 3.86-3.96 (m, 4H, $2CH_2$), 3.16 (s, 4H, $2CH_2$), 2.66-2.61 (m, 4H, $2CH_2$), 1.67-1.60 (m, 4H, $2CH_2$), 1.40-1.37 (m, 4H, $2CH_2$), 0.97-0.94 ppm (m, 6H, $2CH_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.1, 140.6, 138.3, 137.5, 137.3, 133.7, 131.9, 131.3, 129.3, 129.2, 129.1, 129.0, 127.5, 125.2, 125.1, 119.4, 115.1, 108.2, 96.5, 93.2, 93.1, 66.8, 49.1, 35.2, 33.5, (2 signals), 22.4, 22.4, 14.0 (2 signals) ppm. HRMS (ES): m/z: calcd for $C_{43}H_{44}N_{4O}$: 632.3515 $[M^{\cdot}]^+$; found: 632.3511.

Two-photon absorption

TPA cross sections (σ_2) were determined from the two-photon excited fluorescence (TPEF) cross sections ($\sigma_2\Phi$) and the fluorescence emission quantum yield (Φ). TPEF cross sections of 10^{-4} M chloroform solutions were measured relative to fluorescein in 0.01M aqueous NaOH for 715-980 nm, using the well-established method described by Xu and Webb[18] and the appropriate solvent-related refractive index corrections.[25] To span the 690-1000 nm range, a Nd:YLF-pumped Ti:sapphire oscillator was used generating 150 fs pulses at a 76 MHz rate. The excitation was focused into the cuvette through a microscope objective (10X, NA 0.25). The fluorescence was detected in epifluorescence mode via a dichroic mirror (Chroma 675dcxru) and a barrier filter (Chroma e650sp-2p) by a compact CCD spectrometer module BWTek BTC112E. Total fluorescence intensities were obtained by integrating the corrected emission. The quadratic dependence of the fluorescence intensity on the excitation power was checked for each sample and all wavelengths, indicating that the measurements were carried out in intensity regimes where saturation or photodegradation did not occur.

Quantum chemical calculations

Geometry optimizations were carried out at the density functional theory (DFT) level using the M06 exchange correlation (XC) functional[26] and the 6-311G(d) basis set. All structures were characterized as real minima of the potential energy surface on the basis of their vibrational frequencies. Vertical excitation energies and excited state properties were determined using the time-dependent density functional theory (TDDFT) with the M06-2X XC functional and the 6-311G(d) basis set. This functional was shown to provide good results for simulating the excitation spectra of π-conjugated dyes.[27] Solvent effects were included both in geometry optimizations and calculations of the optical properties by using the Polarizable Continuum Model in its Integral Equation Formalism (IEF-PCM).[28] All calculations were performed using the Gaussian 09 package.[29]

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Graphical contents entry:

The pyrrolo[3,2-*b*]pyrrole core was determined to be an efficient linker allowing conjugation of peripheral benzene rings. The resulting dipolar compounds displayed strong solvatochromism of fluorescence while maintaining reasonable two-photon absorption cross-section in polar solvents.