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The effect of rigidity on the emission of quadrupolar strongly polarized dyes†

 Bartosz Szymański,^{ad} Smruti Ranjan Sahoo,^b Rashid Valiev,^c Olena Vakuliuk,^a Piotr Łaski,^d Katarzyna N. Jarzemska,^d Radostaw Kamiński,^{id d} Glib Baryshnikov,^{id *bf} Mohammad B. Teimouri^{id *ae} and Daniel T. Gryko^{id *a}

Hybrid dyes comprising 1,4-dihydropyrrolo[3,2-*b*]pyrrole and two strongly electron-withdrawing benzoxadiazole substituents, differing in their level of planarization, offer an insightful window into the interplay between internal conversion and intersystem crossing as relaxation pathways from the excited state. The emission intensity is strong for non-fused systems whilst it is minimal for fused dyes. Computational evaluation has revealed that internal conversion, and not inter-system crossing, is the main non-radiative process for planar, fused quadrupolar dyes.

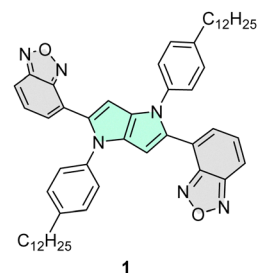
Introduction

Centrosymmetric dyes with acceptor–donor–acceptor (A–D–A) and donor–acceptor–donor (D–A–D) architectures,^{1–5} which form emissive CT states, can display solvatochromism, caused by excited-state symmetry breaking (ES-SB).^{6–10} Many new quadrupolar,^{11–14} centrosymmetric systems have been reported over the last few years, but there has been no consensus on the influence of restricted rotation (rigidity) on the emission properties, ES-SB and thermodynamics of intramolecular charge transfer (ICT).¹⁵

In this regard we hypothesized that it could be possible to directly study the influence of restricted rotation on the fate of quadrupolar dye molecules in the excited state by bridging strongly electron-donating and electron-deficient moieties. Assessing this hypothesis requires two dyes possessing identical, quadrupolar

scaffolds except for their degrees of rigidity. Designing the quadrupolar architectures, we considered several candidates for the electron-rich scaffold, but we eventually decided upon 1,4-dihydropyrrolo[3,2-*b*]pyrrole (DHPP) due to the combination of the following properties: (1) exceptionally high-lying HOMO; (2) straightforward and modular synthesis; (3) possibility of vast structural modification.^{16–18} The combination of these features has been utilized several times, predominantly to decipher the fluorescence of nitro-aromatics.^{19,20} Simultaneously, we reasoned that incorporation of 2,1,3-benzoxadiazole^{21–24} at the strongly conjugated positions 2 and 5 of DHPP represents an optimal choice as an electron-acceptor. The versatility and generality of the multicomponent reaction affording tetraarylpyrrolo[3,2-*b*]pyrroles (TAPPs)²⁵ enabled us to assemble the required quadrupolar dye **1** in just one step (Scheme S1 (ESI†) and Fig. 1). Subsequently the benzo-*c*[1,2,5]oxadiazole-4-carbaldehyde (**2**) was condensed with 2-bromo-4-octadecylaniline (**3**) affording TAPP **5**, which was subjected to intramolecular direct arylation,²⁶ giving almost planar quadrupolar centrosymmetric architecture **6** (Scheme 1).

The photophysical properties of dyes **1** and **6** were studied in solvents of various polarity and in the polycrystalline state


 Fig. 1 Structural formula of centrosymmetric TAPP **1**.

^a Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224, Warsaw, Poland. E-mail: dtgryko@icho.edu.pl

^b Laboratory of Organic Electronics, Department of Science and Technology, Linköping University, SE-60174, Norrköping, Sweden. E-mail: glib.baryshnikov@liu.se

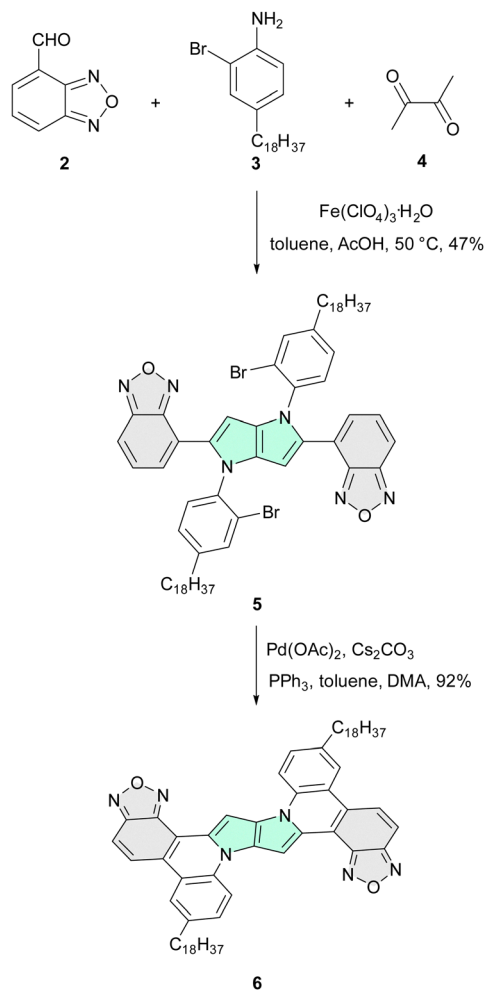
^c Department of Chemistry, University of Helsinki, FI-00014, Helsinki, Finland

^d Department of Chemistry, University of Warsaw, Żwirki i Wigury 101, 02-089 Warsaw, Poland. E-mail: rkaminski85@uw.edu.pl

^e Faculty of Chemistry, Kharazmi University, 15719-14911 Tehran, Iran. E-mail: teimouri@khu.ac.ir

^f Department of Chemistry and Nanomaterials Science, Bohdan Khmelnytsky National University, 18031 Cherkasy, Ukraine

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Scheme 1 Synthesis of dye 6.

(Table 1 and Fig. 2). The presence of the strongly electron-withdrawing benzoxadiazole substituents shifts the absorption and emission about $1900\text{--}2300\text{ cm}^{-1}$ bathochromically with respect to the analogous TAPP possessing two 4-nitrophenyl substituents at positions 2 and 5,¹⁹ and makes TAPP 1 susceptible to changes in solvent polarity. Dye 1 exhibits strong fluorescence in non-polar solvents, characterized by a relatively low Stokes shift (Table 1). However, the fluorescence is

Table 1 Photophysical data for dyes 1 and 6

Dye	Solvent or powder	$\lambda_{\text{abs}}^{\text{max}}/\text{nm}$ ($\epsilon \cdot 10^{-4}/\text{M}^{-1} \text{ cm}^{-1}$)	$\lambda_{\text{em}}^{\text{max}}/\text{nm}$	Φ_{fl}	$\Delta\bar{\nu}/\text{cm}^{-1}$
1	Cyclohexane	499 (29)	553	0.77 ^a	2000
	Toluene	506 (25)	590	0.67 ^a	2800
	THF	501 (25)	623	0.44 ^a	3900
	DCM	504 (23)	673	0.08 ^a	5000
	Cryst. powd.	518	582	0.20 ^b	2100
6	Toluene	354, 452, 580, 626	683, 724 (sh)	0.11 ^c	1330
	THF	351, 448, 576, 637	714	0.03 ^c	1700
	Cryst. powd.	678	743	<0.01 ^b	1300

^a Reference: rhodamine 6G in EtOH ($\Phi_{\text{fl}} = 0.95$). ^b Measured with an integrating sphere. ^c Reference: oxazine 1 in MeOH ($\Phi_{\text{fl}} = 0.11$).

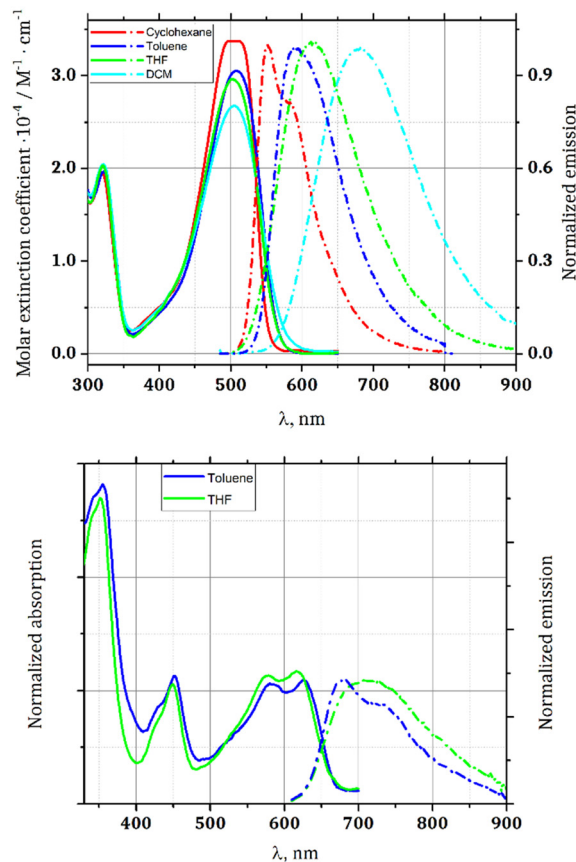


Fig. 2 Absorption (solid lines) and emission (dot-dashed lines) spectra of TAPP 1 (upper) and 6 (lower).

quenched in polar solvents due to the presence of specific non-radiative relaxation pathways, namely charge-transfer-type transitions, and vibrational relaxation of the polar excited state. Solvents such as toluene, tetrahydrofuran (THF) or dichloromethane (DCM) effectively stabilize this state, resulting in larger Stokes shifts (Fig. 2).

On the other hand, rigid and planar (vide infra) dye 6 shows remarkably different characteristics. Predominantly, it has extremely low solubility in the majority of solvents. Careful experiments have proven that in many solvents, it does not form real solutions but rather an ultrafine suspension, which cannot pass through a $0.45\text{ }\mu\text{m}$ syringe filter. Consequently, its photophysical studies were conducted only in toluene and in THF. The large size and planarity of the chromophore inclined us to investigate the possibility to form aggregates. The measurements of the dependence of the absorption on the concentration, performed in toluene, have proven that there is no aggregation within the measured concentration range.

The emission maximum for compound 6 is bathochromically shifted to 683 nm in toluene. Noteworthy, 6 possesses a more rigid chromophore compared to 1 and thus in the excited state it is less exposed to the vibronic relaxation pathways. Hence, compound 6 deactivates with the geometry close to the 1FC^* state with preserved vibronic structure in the emission spectra (in toluene), while for compound 1 the detailed



vibrational structure is lost and the emission spectrum appears as a broad band for most of the cases.

Compound **6** exhibits weak fluorescence, getting even lower in more polar THF, whereas solvatofluorochromism is weaker, but it remains observable (Table 1). It is worth noting that Stokes shifts are significantly lower for compound **6**. They also do not correlate with solvent polarity. For compound **1** they are, however, enormous in polar solvents, providing bathochromic shift of emission (Table 1). Here, planarization causes a strikingly different effect to when nitro groups play the role of electron-withdrawing substituents.²⁷

TAPP **1** crystallizes in the triclinic $P\bar{1}$ space group with two halves of two symmetry-inequivalent molecules in the asymmetric unit (Fig. 3). The C4–C5–C7–N1 and C7–N1–C10–C11 torsion angles are $26.4(5)^\circ$ and $33.0(4)^\circ$, respectively. The distance between C4 and C11 carbon atoms (which are bound in **6**) is $3.098(4)$ Å in the crystal structure of **1**. The main influence on the stability of the crystal structure stems from van der Waals interactions between the long alkyl chains, which results in a layered architecture of the crystal (Fig. 3). There is a hydrogen bond between two TAPP molecules namely C38–H38...N2 (Fig. S11, ESI†).

Having the single crystal structure in hand, we performed solid-state photophysical measurements. As far as the solid-state emission is concerned, both examined quadrupolar dyes, **1** and **6**, exhibit strikingly different properties. In the case of TAPP **1**, there are two emission maxima of a single crystal at room temperature, located around 460 nm and 580 nm, and the

excited-state lifetime is estimated to be $3.800(9)$ ns (Fig. S7, ESI†). For dye **6**, owing to the fused benzene rings when compared to **1**, two emission maxima are notably red-shifted to about 550 nm and 745 nm. As expected, the emission decay of **6** is much faster than that of **1**. The respective room-temperature lifetime is estimated to be *ca.* 1 ns, which is at the accuracy limit of the spectroscopic setup used (Fig. S7, ESI†). It should also be noted that temperature has a greater effect on the emission decay of **6**. When lowering the temperature to 100 K, the emission maximum gets red-shifted ≈ 35 nm, to *ca.* 780 nm with almost no effect on emission lifetime. In the case of dye **1** no significant temperature-dependent spectral changes are observed.

Fluorescence quantum yields in the solid state are markedly different for both compounds. Whereas **1** exhibits a 20% quantum yield, which is considered moderate, dye **6** is almost not fluorescent at all. This corresponds well with results obtained from measurements in various solvents.

The TD DFT optimized excited states (S_1) of both **1** and **6** do not significantly differ from their corresponding ground state (S_0) geometries. Apparently, when going from the S_0 to the S_1 state, it is observed that the dihedral angles change in the range 0.2° – 7.8° and 0.5° – 4.5° between the benzoxiadiazolyl group and DHPP and the benzoalkyl group and DHPP, respectively for non-fused dye **1**; whereas these values are calculated to be nearly zero for fused dye **6**, *i.e.* 0.02° – 0.13° and 0.02° – 0.34° , supporting the rigidity and planarity of dye **6** in the excited state.

Computational calculations using the TD-DFT/PCM/B3LYP-37/6-31G(d,p) formalism were in good agreement with the experimental photophysical properties of dyes **1** and **6** (Table 1). The main absorption and emission bands correspond to the intramolecular HOMO \rightarrow LUMO charge-transfer transition (Fig. 4).

The calculated $S_1 \rightarrow S_0$ radiative rates (k_r) of dye **1** in different solvents are approximately the same (2.0×10^8 s⁻¹),

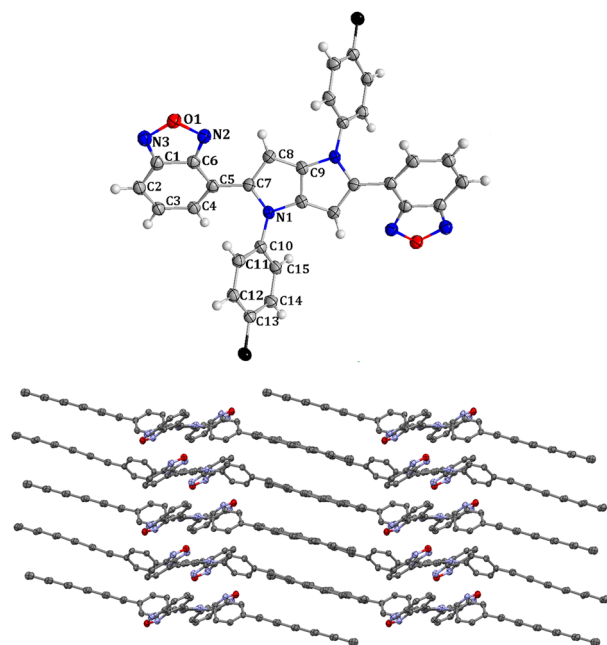


Fig. 3 Molecular structure of **1** (upper). Torsion angles and the distance between C4 and C11 in the **1** crystal structure. Note that ellipsoids correspond to 50% probability of atom location. Alkyl chains and hydrogen atoms are omitted for clarification. Packing in the crystal of **1** (lower). There are some intermolecular interactions between aryl rings, which probably stabilize the structure.

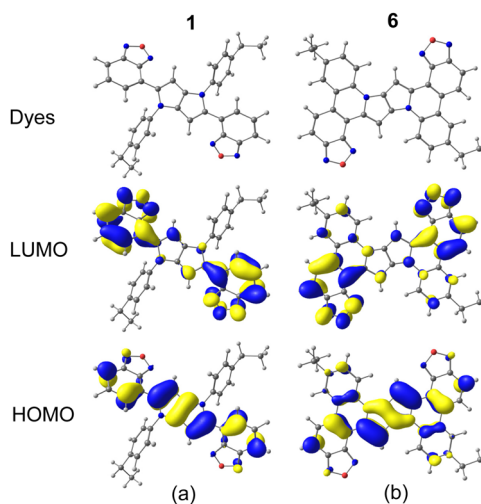


Fig. 4 Calculated optimized ground (S_0) state structures of dye **1** (a) and **6** (b) with ethyl chains and isosurfaces for the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The calculated $E_{\text{HOMO}}/E_{\text{LUMO}}$ values for dye **1** (a) and **6** (b) are $-5.55/-1.99$ eV and $-5.41/-2.21$ eV, respectively. Both $S_0 \rightarrow S_1$ optical absorption and $S_1 \rightarrow S_0$ emission correspond to HOMO \rightarrow LUMO electronic transition.



Table 2 Summary of perturbative spin-orbit coupling excitation calculations, intersystem crossing (ISC), internal conversion (IC) and radiative rate constants of **1** and **6**

Dye	Solvent	E_{S_1}/eV	E_{T_1}/eV	E_{T_2}/eV	SOCME $_{S_1T_1}/\text{cm}^{-1}$	SOCME $_{S_1T_2}/\text{cm}^{-1}$	$k_{\text{ISC}}^{S_1T_1} \times 10^2/\text{s}^{-1}$	$k_r^a \times 10^8/\text{s}^{-1}$	$k_{\text{IC}}^b \times 10^8/\text{s}^{-1}$	$\phi_{\text{fl}}^{\text{theor}}(\phi_{\text{fl}}^{\text{exp}})$
1	Cyclohexane	1.99	1.11	1.62	0.04	0.37	2.06	2.053	1.0	0.61 (0.77)
	Toluene	1.97	1.10	1.61	0.03	0.37	1.35	2.053	1.0	0.58 (0.67)
	THF	1.83	1.05	1.57	0.03	0.39	12.8	2.027	2.3	0.32 (0.44)
	DCM	1.81	1.05	1.56	0.03	0.39	13.7	2.023	2.4	0.31 (0.08)
6	Cyclohexane	1.64	1.02	1.53	0.02	0.00	16.2	0.738	4.3	0.14
	Toluene	1.62	1.01	1.52	0.02	0.00	17.9	0.752	4.7	0.13 (0.11)
	THF	1.53	0.98	1.48	0.01	0.00	27.8	0.805	7.0	0.10 (0.03)
	DCM	1.52	0.98	1.48	0.01	0.00	29.1	0.810	7.5	0.09 (< 0.01)

while for fused dye **6** the radiative rate is approximately three times smaller ($0.7\text{--}0.8 \times 10^8 \text{ s}^{-1}$). We found two triplet states (T_1 and T_2) energetically lower than the S_1 state for both dyes. The spin-orbit coupling matrix elements (SOCMEs) between S_1 and T_1 states for both **1** and **6**, however, are negligibly small (less than 0.05 cm^{-1}) while the $S_1\text{--}T_1$ energy gap is considerable ($0.7\text{--}0.9 \text{ eV}$ for **1** and near 0.6 eV for **6**) which results in a calculated rate of $S_1 \rightarrow T_1$ intersystem crossing ($k_{\text{ISC}}^{S_1T_1}$) of $10^2\text{--}10^3 \text{ s}^{-1}$ order of magnitude (Table 2 and Table S8, ESI[†]), *i.e.* uncompetitive with the radiative rate. At the same time, the $S_1\text{--}T_2$ gap is much smaller for both **1** and **6**, while SOCME between the S_1 and T_2 states for **1** is large (near 0.4 cm^{-1}). This results in $k_{\text{ISC}}^{S_1T_2}$ for **1** being in region of $0.36\text{--}2.0 \times 10^8 \text{ s}^{-1}$, *i.e.* it is comparable with the radiative rate constant. However, for compound **6** the SOCME between the S_1 and T_2 states is predicted to be zero, which corresponds to a zero rate constant for $k_{\text{ISC}}^{S_1T_2}$. This means that fluorescence quenching for dye **6** originates from $S_1\text{--}S_0$ internal conversion (IC). Indeed, our calculations predict k_{IC} for compound **6** to increase with an increase of solvent polarity from $4.3 \times 10^8 \text{ s}^{-1}$ in cyclohexane to $7.5 \times 10^8 \text{ s}^{-1}$ in DCM. For compound **1**, internal conversion also significantly contributes to fluorescence quenching and demonstrates a similar solvent polarity dependence as for fused dye **6**. The calculated values of fluorescence quantum yield ($\phi_{\text{fl}}^{\text{theor}}$) estimated as a relation between radiative rate and the sum of radiative and all non-radiative rate constants finally demonstrates a good agreement with the experimental measurements (Table 2 and Table S8, ESI[†]).

Conclusions

In conclusion, by planarization of the geometry of highly polarized, centrosymmetric dyes, it is possible to gain control over the fate of the molecular excited state. Furthermore, our observations indicate that while balanced donor-acceptor coupling ensures fast radiative deactivation and slow ISC essential for large fluorescence quantum yields, planarization changes this balance towards IC. Planarization reduces spin-orbit coupling matrix elements between the singlet and triplet excited states to essentially zero, shifting the main mechanism of non-radiative deactivation from S_1 to S_0 from intersystem crossing to internal conversion. These mechanistic paradigms set important design principles for molecular photonics and electronics.

Author contributions

Conceptualization: D. T. G. and M. B. T.; investigation: B. S., O. V., M. B. T., P. Ł., S. R. S., R. V.; supervision: D. T. G., G. B., R. K., K. N. J.; visualization: D. T. G., B. S., P. Ł.; writing – original draft: B. S., D. T. G., O. V., G. B., P. Ł., R. K., K. N. J.; writing – review and editing: D. T. G., O. V., R. K., K. N. J., G. B.

Conflicts of interest

There are no conflicts to declare.

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