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Azophenine as Central Core for Efficient Light Harvesting Devices

Hu Lei, Paul-Ludovic Karsenti, and Pierre D. Harvey*

Département de chimie, Université de Sherbrooke, PQ, Canada J1K 2R1

Abstract. The notoriously non-luminescent uncycled azophenine (**Q**) was harnessed with Bodipy and zinc(II)porphyrin antennas to probe its fluorescence properties, its ability to act as a singlet excited state energy acceptor and to mediate the transfer. Two near-IR emissions are depicted from time-resolved fluorescence spectroscopy, which are most likely due to the presence of tautomers of very similar calculated total energies (350 cm^{-1} ; DFT; B3LYP). The rates for energy transfer, $k_{\text{ET}}(S_1)$, for ¹Bodipy* \rightarrow **Q** are in the order of 10^{10} - 10^{11} s^{-1} and are surprisingly fast when considering the low absorptivity properties of the lowest energy charge transfer excited state of azophenine. The rational is provided by the calculated frontier MOs which show atomic contributions in the C₆H₄C≡CC₆H₄ arms, thus favoring the double electron exchange mechanism. In the mixed-antenna Bodipy-porphyrin star molecule, the rate for ¹Bodipy* \rightarrow porphyrin has also been evaluated (~ $16 \times 10^{10} \text{ s}^{-1}$) and is among the fastest rates reported for Bodipy-zinc(II)porphyrin pairs. This astonishing result is again explained from the atomic contributions of the C₆H₄C≡CC₆H₄ and C≡CC₆H₄ arms thus favoring the Dexter process, a process found here for the first time sensitively temperature-dependent. In overall, the azophenine turns out to be excellent for electronic communication.



Graphic art

Keywords: Dexter energy transfer · FRET · azophenine · porphyrin · Bodipy · star-shape

Introduction

Azophenine (**1**, Figure 1) and its various cyclized and uncyclized organic derivatives and coordination complexes are renowned to be redox active^[1-9] and on some occasions, catalytic activity was reported ^[7, 10]. Noteworthy, the ability of tetraazalene radical bridging ligands to mediate exceptionally strong magnetic exchange coupling across a range of transition metal complexes was also demonstrated^[1, 11]. However, these uncycled dyes are also known to be notoriously non-luminescent. This silent trait changes when the flexible core is rigidified by forming cycles, most of the time at the N^N centers^[12-14].We have recently demonstrated that it is possible to observe multiple weak emissions from upper excited states of the four arms $\pi\pi^*$ manifolds (fluorescence and phosphorescence) in the visible range, and lower charge transfer excited state (fluorescence) in the near-IR region, in either fluid solution or in the solid state at room temperature for uncycled dyes^[15].



Figure 1. Structure of 1 and uncycled azophenines stressing on the evolution $(1 \rightarrow 2 \rightarrow 3a \rightarrow 3b \rightarrow 3c)$ of their emissive traits (Boc = tert-butyloxycarbonyl).

The secret behind this notable photophysical improvement towards detectable fluorescence and phosphorescence at room temperature in fluid solution stems from the anchoring of large groups such as truxene and $C_6H_5C\equiv CPt(PR_3)_2C\equiv C$ - at the *para*-position of the phenyl groups of azaphenine (X in Figure 1), which slows down the rotations about the N-C single bonds, and hence providing extra undesired efficient non-radiative relaxation pathways.

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Azophenine (1) can also be considered as a functional central core of a star shaped molecules, although literature shows that this was never perceived this way until our recent works^[15-16]. However, no photo-induced electron or energy transfers were observed in these cases. Conversely, there are multiple studies on energy transfer processes in porphyrin-^{[17-} ^{25]} and Bodipy-^[26-35] containing branches of star shaped molecules and dendrimers, making these chromophores, dyes of choice for probing the interactions between the branches and the functional central core. In order to promote the energy transfer operating through a Dexter mechanism (i.e. double electron exchange), a conjugated system is required. The imine function can promote π -conjugation. Concurrently, our team and other groups have also demonstrated that electronic communication through a -(NR)- linker (R = H; alkyl) is possible^[36-37]. The azophenine dye **1** contains both the needed imine and amine linkages. The biggest curiosity in the scarcely reported photophysical properties of the uncycled azophenine chromophore^[15-16], is the recently reported ON-OFF switching of emission properties of by changing the dihedral angle made by the central quinone diimine (**Q**) plane and the N-C₆H₄ one upon the removal of the Boc group in 2 to form 3a (Figure 1; *i.e.* $2 \rightarrow$ **3a**; Boc \rightarrow H; large angle \rightarrow small angle)^[38]. Despite of this rather interesting phenomena, no explanation was offered at that time. In an attempt to provide an explanation on the basis of the suspected change in π -conjugation properties, the singlet-singlet energy transfer processes, here promoting the Dexter process, was investigated using zinc(II)porphyrin and Bodipy as antennas, and the central azophenine (\mathbf{Q}) as the acceptor (Figure 2).





line with the conclusion drawn by electron spin resonance^[11, 39], and a valuable fluorescent chromophore indicating that this dye is not photophysically silent as previously believed.

Results and Discussion

Synthesis. The target polyads are prepared according to pathways shown in Schemes 1 and 2. **B4Q** (Scheme 1) proceeds from compound $3a^{[38]}$. After the deprotection of the ethynyl linkers, compound **4** is obtained. The latter intermediate is then coupled to the known iodo-compound $5^{[40]}$ in a 1:4 ratio under copper-free Sonogashira conditions in order to obtain the desired **B4Q** with a yield of 50%. The synthesis of **B2Q**, and **P2B2Q** is performed using the same precursors $5^{[40]}$ and $6^{[40]}$. The comparison donor molecule **Por** is obtained from the known compound $8^{[41]}$. The formation of **B4Q**, **P2B2Q** and **B2Q** was confirmed by mass spectrometry and ¹H NMR spectroscopy. The characteristic NMR signals from the Bodipy, porphyrin and the central azophenine units are accompanied by the disappearance of the resonance at 3.1 ppm from the terminal alkynyl hydrogen present in **4** and **6**, thus implying the success of the coupling reaction.



Scheme 1. Reaction path to prepare B₄Q. *i*) K₂CO₃, DCM/MeOH, R.T., 91%^[16]; *ii*) Pd(dba)₃, Ph₃As, Et₃N, 50%.



Scheme 2. Reaction paths for the synthesis of B_2Q , P_2B_2Q and Por. i) Pd(dba)₃, Ph₃As, Et₃N, 52-60%; ii) K₂CO₃, DCM/MeOH, R.T, 92%; iii) Zn(AcO)₂, MeOH/DCM, 2h, 95%; iv) ethynylbenzene, PdCl₂(PPh₃)₂, CuI, Et₃N, 82%. Ar = 3,5-(*t*-butyl)₂C₆H₃.

Azophenine is known to exhibit tautomeric forms,^[42-44] with an exchange rate of ~720 s⁻¹ in solution at 298 K and an activation barrier of 47.5 \pm 2.5 kJ mol⁻¹ in THF^[44]. Consequently, **P₂B₂Q** may exist under two tautomeric forms as well (Scheme 3).



Scheme 3. Tautomerization of P_2B_2Q (Ar = 3,5-(*t*-butyl)₂C₆H₃).

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Geometry optimization (DFT; B3LYP) was used to address *tautomer 1* (porphyrin unit on the imine-arms) and *tautomer 2* (porphyrin unit on the amine-arms), as well as the structures for B_4Q and B_2Q . The latter dyads can also exist in tautomeric forms but these species were not investigated for reasons that are obvious below.

Optimized geometry. The optimized geometry of **B**₄**Q**, **B**₂**Q** and *tautomer 1* and *tautomer* 2 of **P**₂**B**₂**Q** are all treated as *isomorph 1* (Scheme 4) for sake of consistency, and are presented in Figure 3 stressing on the dihedral angles made by the various planes in order to address the relative ability for π -conjugation. The activation barrier is ~10 kJ/mol (SI).



Scheme 4. Representations of the possible equilibrium between *isomorph 1* (more stable) and *isomorph 2*.^[46,47] The calculated energy map for the interconversion is placed in the SI.

The key features are as follow: the C₆H₄-C=C-C₆H₄ bridge is quasi-planar with a dihedral angle varying from 0.5 to 6.5°, the porphyrin-C=C-C₆H₄ angles also approach planarity with a largest value of 12°, and the Bodipy-C₆H₄ angles make a quasi-right angle (between 85 and 88°). These computational outcomes are expected. The dihedral angles made by the C₆H₄-NH-quinone diimine and by the C₆H₄-N=quinone diimine respectively range from ~30 to 33° and ~51 to 55°. These ranges are exactly what is expected for this type of steric interactions^[15, 45]. The longer single N-C bond with respect to N=C one allows for less steric hindrance between the ortho-hydrogens and the central quinone diimine. Therefore, a smaller C₆H₄-NH-quinone diimine dihedral angle is possible. Consequently, the electronic communication through the -NH- bridge^[36-37] is favoured with the smaller angle. The total energies computed for *tautomer 1* (-12309.82781) and *tautomer 2* (-12309.82960 a.u.) for **P2B2Q** are quasi-identical with only a difference of 350 cm⁻¹ (0.0489 eV). This particularly small difference strongly suggests that both forms must exist in solution and that their photophysical responses must be taken into account.

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Figure 3. Optimized geometries of B_2Q , B_4Q and P_2B_2Q (*tautomer 1* and *tautomer 2*) showing the dihedral angles made by various planes.

Finally, azophenine (compound 1) exits under two isomorphous forms in the solid state [46-^{47]}, and one may wonder whether these forms (*isomorph 1* and *isomorph 2*; Scheme 4) also leave their own photophysical signatures. The calculated energy difference is only 0.0001206 a.u. (i.e. 0.00328 eV; 26.5 cm⁻¹; optimized geometry by DFT; see SI for detail) indicating that the relative population is ~ 50 %. Because the interconversion requires the rotation of two phenyl groups either at once or sequentially, the process may be slow at room temperature but should be completely frozen down at 77 K. Consequently, the presence of two emission lifetimes for a seemingly single emission band and for a symmetric azophenine containing four identical arms can only be explained by their presence. Indeed, this was the case for compound $3a^{[38]}$. TDDFT compute quasi-identical simulated spectra for *isomorphs 1* and 2 for compounds 1 and 3a (SI) suggesting that these species are not easily observed by steady sate spectroscopy. Considering the presence of tautomers and isomorphs, one should unavoidably consider the uncycled azophenines as a complex system described as (*tautomer 1/isomorph 1*) \leftrightarrow (*tautomer 1/isomorph 2*) \leftrightarrow (*tautomer* $2/isomorph 2) \leftrightarrow (tautomer 2/isomorph 1) \leftrightarrow$, in both the ground and excited states with a relative population of ~25 %. The consequence for this feature is that the analysis of the

energy transfer processes needs to be addressed in a global manner. Noteworthy, no H/D exchange experiment was performed since this was not the aim of this study.

Absorption spectroscopy. Figure 4 exhibits the absorption and fluorescence spectra for selected compounds. The absorption data are listed in Table 1. The spectra for **5** and **Por** at 298 K are placed in SI for comparison purposes. The absorption band of **B**₂**Q** at 323 nm is assigned to a π - π * transition similar to that observed for **3a** (azophenine core). The peak at 525 nm arises from the lowest-energy π - π * excited state of the Bodipy unit. The **B**₄**Q** absorption spectrum is expectedly very similar to that of **B**₂**Q**, and so are the assignments. The 495 and 525 nm-bands arise from the Bodipy unit and the one placed at 326 nm mainly stems from the azophenine center.



Figure 4. Top left: absorption spectra of **3a** (black), B_2Q (red), P_2B_2Q (green), B_4Q (blue) in 2MeTHF at 298 K. Top right: fluorescence spectra of **5** (black), B_2Q (red) and B_4Q (blue) in 2MeTHF at 298 K. Bottom left: emission spectra of **Por** (blue), **5** (black) and P_2B_2Q (red) in 2MeTHF at 298 K. Bottom right: fluorescence spectra for B_2Q (red), B_4Q (blue) and P_2B_2Q (green) in 2MeTHF at 77 K, the spectrum for P_2B_2Q is filled with different colors to distinguish the origin of the various fluorescences, respectively from Bodipy, zinc(II)porphyin and azophenine.

	$\lambda_{abs} (nm) (\epsilon (x \ 10^{-4} \ M^{-1} cm^{-1}))$
Por	308 (2.1), 420 (6.0), 439 (44.9), 574 (1.6), 622 (2.8)
5	378 (0.8), 496 (2.6), 525 (8.0),
B ₂ Q	326 (7.3), 395 (3.1), 496 (4.4), 525 (10.8)
B4Q	335 (5.4), 398 (2.7), 496 (4.6), 525 (11.2)
P_2B_2Q	327 (8.1), 445 (36.8), 496 (6.0), 575 (2.5), 633 (5.8)

Table 1. UV-vis absorption data for the polyads and models in 2MeTHF at 298 K.

The comparison of the absorption spectra of B_2Q , B_4Q and P_2B_2Q with their comparison molecules **3a**, **5** and **Por**, indicates that their spectra are slightly shifted from the spectra of the individual comparison molecules. This result indicates the presence of interchromophore π -conjugation or electronic interactions. Moreover, the expected broad azophenine band in the 400-450 nm range for B_2Q , B_4Q and P_2B_2Q was not depicted. This is likely due to a spectral overlap with the strong bands of the Bodipy and porphyrin units. The expected Q bands of the porphyrin units are observed at 575 and 632 nm (298 K) and are readily assigned on the basis of a comparison with those for **Por** (Figure 4). In addition, a weak tail (298 K) and a shoulder (77 K) are noticed at ~675 nm for **P_2B_2Q** (Figure 5, green arrows).



Figure 5. Comparison of the absorption spectra of Por and P₂B₂Q in 2MeTHF.

This feature along with the unusual red shift of the low energy Q band upon cooling (20 nm instead of 6 nm for **Por**) strongly suggest that a signal is growing with the cooling at \sim 675 and thus influencing the overall band shapes. A CT band of non-zero oscillator

strength values is most likely at the origin of this phenomenon (detail below). In order to shine light on this unusual behaviour, one should consider the tautomerization behaviour of the azophenine core (-N-H•••N= $\leftrightarrow =$ N•••H-N-)^[42-44]. Moreover, it is again known that azophenine exists into two isomorphic forms due to a change in the dihedral angles made by the C₆H₄ planes vs the quinone diimine one^[46-47]. These possible explanations are explored by DFT and TDDFT computations for **P**₂**B**₂**Q**.

The interpretation of the absorption and fluorescence spectra is addressed by DFT (B3LYP) and TDDFT calculations. The representations of the atomic contributions of frontier MOs for **B**₂**Q**, **B**₄**Q** and **P**₂**B**₂**Q** (optimized geometries) are in Figures 6 and 7, and this series can be divided into **B**₂**Q** and **B**₄**Q** *vs* **P**₂**B**₂**Q**. The HOMO and LUMO for **B**₂**Q** and **B**₄**Q** exhibits contributions on the azophenine core and on the four arms with various amounts almost reaching the Bodipy dye.



Figure 6. Representations of the frontier MOs of B_2Q (up) and B_4Q (down) using a THF solvent field (energies in eV). More frontier MOs are placed in the SI. Note that the Bodipy chromophore exhibits localized atomic contributions whereas the azophenine shows contributions in the centers and the arms.

Based on the change in atomic contributions, the HOMO \rightarrow LUMO transitions for **B**₂**Q**

creates a C=N (imine)-to-NH (amine) charge transfer (CT) state, and for **B4Q**, it generates a NH (amine)-to-C=N (imine) CT manifold. This change in CT direction is unambiguously due to the substituent effect (SiMe₃ vs Bodipy), and has no consequence on the end conclusion (the rate for energy transfers, ¹Bodipy* \rightarrow azophenine (**Q**) are quite similar for these two cases; details below). Moreover, the upper energy MO levels (see for example HOMO-1 and LUMO+1 for **B**₂**Q**) are localized π and π^* levels. So, a spin-allowed HOMO-1 \rightarrow LUMO+1 transition generates a localized ¹Bodipy* excited state. This situation is the same for **B4Q** (Figure 6, bottom). TDDFT computations place the lowest energy absorption peaks at respectively 621 and 638 nm for **B**₂**Q** and **B**₄**Q** with an oscillator strength, f, of 0 (Table 2 for the first 5 transitions, see SI for the first 100 transitions). Experimentally, no absorption signal is observed in the 500-750 nm range. Moreover, the lowest energy fluorescence band starting at ~660 nm is noted (below) for both compounds right where it is expected from the TDDFT predictions. In conclusion, these calculations corroborate the presence of these silent CT manifolds, and that **B**₂**Q** and **B**₄**Q** are energy transfer dyads (Bodipy = donor, azophenine = central acceptor).

Table 2. Calculated positions of the pure electronic transitions, oscillator strengths (f), and major contributions for B_2Q and B_4Q .

no	λ(nm)	f	Major contributions for B ₂ Q (%)
1	625	0	HOMO→LUMO (98)
2	543	0.629	H-3→LUMO (98)
3	526	0.000	H-1→LUMO (100)
4	526	0.000	H-2→LUMO (100)
5	480	1.046	H-4→LUMO (92)
no	λ(nm)	f	Major contributions for B4Q (%)
1	638	0	HOMO→LUMO (98)
2	569	0.874	H-5→LUMO (97)
3	537	0.000	H-2→LUMO (100)
4	537	0.000	H-1→LUMO (100)
5	5 25	0	

 P_2B_2Q may exist in two tautomeric forms which may have their own signatures. The analysis of the atomic contributions of P_2B_2Q MOs reports a slightly different situation (Figure 7).



Figure 7. Representations of selected frontier MOs of P_2B_2Q (16 MOs, *tautomer 1*: up; 4 MOs, *tautomer 2*; down) using a THF solvent field (energies in eV). More frontier MOs are placed in the SI.

The atomic contributions of the HOMO in *tautomer 1* spread from the porphyrin units (major) through the C=CC₆H₄ arms (major), reaching the central azophenine (minor). Conversely, the atomic contributions on the LUMO spread from the azophenine (major), to the C=CC₆H₄ arms (medium) to the porphyrin residues (minor). So, a HOMO \rightarrow LUMO also creates a CT state (porphyrin-to-azophenine) mainly localized on the quinone diimine line heavily involving the porphyrin fragments. This outcome is due to a nearly planar geometry of the NC₆H₄C=C-porphyrin fragment (from geometry optimizations) favouring π -conjugation, and consequently the position of the CT signal is expected to be red-shifted

with respect to B_2Q and B_4Q . The upper energy MOs are composed of localized π or π^* systems on the porphyrin units (HOMO-4 and -3; LUMO+5 and +6), and on the Bodipy (HOMO-5 and -6; LUMO+2 and +3). These calculations suggest that P_2B_2Q is a triad composed of Bodipy (higher), porphyrin (medium) and azophenine (lower energy). The description of the MOs for *tautomer 2* is the same so far. At this point, one can readily predict the presence of a strong MO coupling between the porphyrin units and azophenine as they share a common segment, i.e. the porphyrin itself.

TDDFT computes the position of the low energy bands with higher f values at 577 and 721 nm for *tautomer 1* and 552, 585 and 681 nm for *tautomer 2* (Table 3).

Table 3. Calculated positions of the pure electronic transitions, oscillator strengths (f), and major contributions for P_2B_2Q in *tautomer* 1 (top) and *tautomer* 2 (bottoms) forms.

no	$\lambda(nm)$	f	Major contributions for P_2B_2Q (%; porphyrin on the imine arm)
1	721	1.602	$HOMO \rightarrow LUMO (95)$
2	707	0.011	$H-2 \rightarrow LUMO (10), H-1 \rightarrow LUMO (86)$
3	601	0.000	$H-2 \rightarrow LUMO (81), H-1 \rightarrow LUMO (12)$
4	581	0.005	H-3 \rightarrow LUMO (35), H-3 \rightarrow L+1 (12), H-1 \rightarrow L+6 (18), HOMO \rightarrow L+6 (29)
5	581	0.004	H-4 \rightarrow LUMO (35), H-4 \rightarrow L+1 (12), H-1 \rightarrow L+5 (23), HOMO \rightarrow L+5 (23)
6	577	0.017	$H-3 \rightarrow L+6 (12), H-1 \rightarrow L+4 (18), HOMO \rightarrow L+1 (56)$
7	575	0.310	$H-4 \rightarrow L+5 (10), H-1 \rightarrow L+1 (48), HOMO \rightarrow L+4 (28)$
8	545	0.001	$H-1 \to L+2$ (38), HOMO $\to L+2$ (61)
9	542	0.000	$H-1 \rightarrow L+3$ (27), HOMO $\rightarrow L+3$ (73)
10	540	0.000	$H-5 \rightarrow LUMO (100)$
no	λ (nm)	f	Major contributions P_2B_2Q (%; porphyrin on the amine arm)
1	711	0.004	HOMO→LUMO (91)
2	681	0.909	H-1→LUMO (95)
2	505	0.00	$H_{1} \to H_{1} + A_{1} (17) HOMO \to H_{1} + I_{1} (2)$

3	585	0.662	$H-1 \rightarrow L+4 (17), HOMO \rightarrow L+1 (62)$
4	580	0.004	H-1 \rightarrow L+1 (45), HOMO \rightarrow L+4 (28)
5	576	0.008	$H-3 \rightarrow LUMO(21), H-3 \rightarrow L+1(15), H-1 \rightarrow L+5(26), HOMO \rightarrow L+5(28)$
6	576	0.008	H-2 \rightarrow LUMO (21), H-2 \rightarrow L+1 (15), H-1 \rightarrow L+6 (24), HOMO \rightarrow L+6 (29)
7	560	0.008	H-6→LUMO (83)
8	554	0.032	H-1 \rightarrow L+2 (29), HOMO \rightarrow L+2 (62)
9	552	1.097	H-7→LUMO (89)
10	545	0.000	$H-1\rightarrow L+3$ (26), $HOMO\rightarrow L+3$ (64)

^aThe simulated absorption spectra are placed in the SI for convenience.

The 577 nm transition (H-3 \rightarrow L+6 (12), H-1 \rightarrow L+4 (18), HOMO \rightarrow L+1 (56%)) is a quasilocalized $\pi\pi^*$ transition of the porphyrin pendent group (*i.e.* Q band) slightly mixed with the central azophenine core. Experimentally, this band is indeed observed at 575 nm at 298 K (Table 1), and a more intense peak (with respect to the 575 nm band) is depicted at 632 (298) and 652 nm (77 K), which are undoubtedly the two Q bands. Noteworthy, a shoulder or a tail in the vicinity of 700 nm is noticed. The calculated 721 nm transition is the porphyrin-to-azophenine CT for *tautomer 1* but with f = 1.6. For *tautomer 2*, TDDFT computations predict a peak at 681 nm with f = 0.9 (H-1 \rightarrow LUMO (95%)), and a much weaker one at 711 nm with f = 0.004 (HOMO \rightarrow LUMO (91%)). Both excited states are CT manifolds. Experimentally again, a shoulder at 675 nm is depicted (Figure 5), and this value compares favourably to calculated 681 nm transition. Noteworthy, the temperature dependence of the low energy Q-band (632 vs 652 nm), also supports the hypothesis that two tautomers are present in solution. Moreover, TRES depicts two distinct fluorescences in the near-IR region (below). These fluorescence bands at 77 K start at ~680 and ~700 nm, which compare more favourably to the computed 711 (tautomer 2) and 721 nm (*tautomer 1*) values.

Fluorescence spectroscopy and lifetimes. Figures 4 (frames B, C, and D) and 8 exhibit the fluorescence spectra of the polyads. The corresponding spectra for the models **Por** and **5** are placed in the SI. P_2B_2Q exhibits the three expected fluorescence bands: Bodipy (~540 nm), zinc(II)porphyrin (~620 nm) and azophenine (~750 nm).



Figure 8. Absorption (black), excitation (blue, turquoise) and emission spectra (green, red, olive) for P₂B₂Q in 2MeTHF.

Knowing from the literature that azophenine is a non-luminescent chromophore, then the fluorescence quantum yields, Φ_F , for the recorded near-IR CT emission must be small (note that Φ_F is not accessible due to the detection limit of the integration sphere and the absence of appropriate comparative standard). The comparison of the relative intensity of the Bodipy vs porphyrin vs CT azophenine bands indicates that Φ_F for Bodipy and porphyrin must be small as well, so their excited states must be quenched. This quenching is readily attributed to singlet energy transfer over electron transfer based on fs transient absorption spectroscopy (TAS; the transient signals are the same in the polyads vs those for the comparison molecules, below). The fact that the excitation spectra for all the fluorescence match those for the absorption indicates that these energy transfer processes are efficient. In order to extract the rates for singlet energy transfer, k_{ET}(S₁), the excited state lifetimes, τ_e , for each chromophore has been measured by time-resolved spectroscopy: TCSPC, Streak camera, and fs TAS, for $\tau_e > -1$ ns (FWHM of the excitation pulse ~90 ps), IRF < τ_e <-1 ns (IRF = Instrument Response Function, in this case 9-10 ps), and $\tau_e < -10$ ps (IRF ~ 150 \pm 35 fs, delay line ~8 ns), respectively.

	29	98 K		77 K
	$\lambda_{em} (nm)$	$ au_{ m F}$	$\lambda_{em}(nm)$	$ au_{ m F}$
5	538	4.67 ns	532	5.73 ns
Por	627	2.18 ns	627	2.76 ns
	541	~ 19 ps	537	~ 22 ps (major component),
B ₂ Q				83 ps (minor component)
	b,c	d	750	930 ps
D O	545	~ 22 ps	535	~ 26 ps
B4Q	b,c	d	750	475 ps
	540	~ 12 ps	533	~ 16 ps
PaBaO	636	d	646	d
1 2D2Q	b,c	d	750	170 ps (major component),
				430 ps (minor component)

Table 4	4.]	Fluorescence	data	for 5	, Por	B_2Q	P_2B_2C) and B 4() in 2MeTHF. ³
							/		

^aAll ns τ_F data were measured by TCSPC (uncertainties ± 0.05 ns); all ps τ_F data were measured by Streak camera (the Streak camera results are placed in the Supporting Information; IRF ~9-10 ps; uncertainties $\pm 10\%$). ^bIll defined and weak by Streak. ^cNot observed by steady state. ^dVery weak in the Streak camera measurements.

The fluorescence data (i.e. τ_F) for the polyads and comparison molecules are provided in Table 4 and the extracted time-resolved fluorescence spectra (Streak camera) for the polyads are shown in Figure 1. Two main observations can be made. First, in comparison with the model compound **Por** and **5**, τ_F for the Bodipy chromophore the quenching has indeed decreased from 4-6 ns down to 12-26 ps at both temperatures (one minor component is found at 83 ps). Second, τ_F for the porphyrin unit is < ~9-10 ps, so fs TAS is used below. For **P2B2Q**, two species are depicted with different signatures (λ_{max} and τ_F). These species are most likely due to *tautomer 1* and *tautomer 2* in their excited states. Based on the calculated positions of their electronic transitions respectively at 721 and 711 nm (Table 3), these emission maxima are found at $\lambda_{max} = 745$ (blue line) and 725 nm (green line, Figure 9). Their τ_F values at 77 K (168 and 426 ps, respectively) are shorter than those for **B2Q** (930 ps) **B4Q** (475 ps). This trend is consistent with the "loose bolt" effect; as the mass of the substituents increases, k_{IC} (non-radiative rate constant for internal conversion) increases, and τ_F decreases.



Figure 1. Uncorrected decay associated spectra obtained by global analysis and τ_F data for **B₂Q**, **B₄Q** and **P₂B₂Q** in 2MeTHF (Streak Camera, $\lambda_{ex} = 500$ nm). The τ_F data are rounded off in Table 4 in order to take into account the uncertainties.

The TAS of the comparison compounds **5**, **Por**, and **3a** are provided in Figure 10. For **5** and **Por**, the extracted 1.64 and 8.5 ns components, respectively, are most likely their S₁ excited

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state lifetimes deduced from the TRES data (i.e. respectively $\tau_F = 2.18$ and 4.67 ns). The discrepancy is not fully understood at this time. For **Por**, the strong 25 ns component is the T₁ species but this lifetime value cannot be considered accurate since it exceeds the optical delay line (8 ns). In addition, a weak component of 3.4 ps is also apparent in this case (green trace). This non-luminescent species has been documented before and consists of a solvent-Zn assembly. The time scale for relaxation depends on the solvent and may range from several ps to 50 ps^[48]. For **5**, the 46 ps component may be a metastable conformer which deactivates in the ps time scale. This phenomenon has been fully described by Lindsey and collaborators^[49]. For compound **3a**, the two transient components (1.2 and 4.4 ps) reproduce well the previously reported data (1.1 and 4.9 ps) for the same compound^[38].



Figure 2. Top: fs TAS of 5 (left), Por (middle), and 3a (right) in 2MeTHF at 298 K. Bottom: fs TAS of B_2Q (left), B_4Q (middle), and P_2B_2Q (right) in 2MeTHF at 298 K. The positive and negative signals are respectively the transient and bleach absorptions.

For B_2Q and B_4Q , two short-lived components are depicted in the ps time scale exhibiting similar TAS profiles as that found for 5 (Figure 10). The key issue is the decrease in lifetimes going from 8.6 ns and 46 ps (5) down to 22 and 5.7 ps (B_2Q) and to 19 and 4.2 ps (B_4Q). This behaviour is consistent with a singlet energy transfer process. The 22 and

19 ps values favorably compare with that measured by Streak camera (respectively ~19 and ~22 ps; Table 4). Note that the shorter ps components in the fs TAS experiments (5.7 and 4.2 ps) could not be detected by Streak camera as the IRF was ~9-10 ps. The $k_{\text{ET}}(S_1)$ values can be extracted from $k_{\text{ET}}(S_1) = (1/\tau_F) - (1/\tau_F^\circ)$ where τ_F and τ_F° are the singlet lifetimes of the energy donor in the absence of an energy acceptor, respectively^[50]. Using τ_F° for **5** (4.67 ns) and **Por** (2.18 ns; TCSPC data, Table 4) for the long component, the corresponding $k_{\text{ET}}(S_1)$ are obtained (Table 5).

	Process	<i>k</i> _{ET} (S ₁) (s ⁻¹) 298 K ^b	$k_{\rm ET}({ m S}_1)~({ m s}^{-1})~77~{ m K}^{ m c}$
B ₂ Q	¹ Bodipy*→Q	15 x 10^{10} (short comp.) 4.6 x 10^{10} (long comp.)	4.5 x 10 ¹⁰ (major) ^d 1.2 x 10 ¹⁰ (minor)
B4Q	¹ Bodipy*→Q	22×10^{10} (short comp.) 5.2 x 10^{10} (long comp.)	3.8 x 10 ¹⁰
P2B2Q	¹ Bodipy*→Por. + ¹ Bodipy*→Q	38 x 10 ¹⁰	~6.3 x 10 ¹⁰
	¹ Porphyrin* \rightarrow Q	10 x 10 ¹⁰	too weak

Table 5. $k_{\text{ET}}(S_1)$ data for **B**₂**Q**, **P**₂**B**₂**Q** and **B**₄**Q**.^a

^aAll data were measured in 2MeTHF, samples were prepared in glove box. Q = azophenine. ^bBased on fs TAS data (IRF ~ 150 ± 35 fs; uncertainties ± 10%). ^cBased on the data measured by Streak camera (IRF ~ 10 ps; uncertainties ± 10% based on multiple measurements). ^dIt is suggested that these two components arise from the presence of two tautomers.

Moreover, assuming that the 46 ps species for **5** is associated with those in the vicinity of ~5 ps for **B**₂**Q** and **B**₄**Q**, then their $k_{\text{ET}}(S_1)$ can be estimated as well. No fs TAS data can be obtained at 77 K for obvious set-up reasons. The $k_{\text{ET}}(S_1)$ data are extracted from the Streak camera measurements only. For **B**₂**Q** and **B**₄**Q**, four observations are made:

-First, the The $k_{\text{ET}}(S_1)$ values are comparable to each other, meaning that the number of Bodipy unit attached to the azophenine core has a minimal effect on the antenna properties of the star azophenine molecule.

-Second, a decrease in $k_{\text{ET}}(S_1)$ occurs upon cooling. This is explained by a decrease in the J-integral (normalized spectral overlap between the fluorescence band of the donor and the absorption spectrum of the acceptor) as the electronic band sharpen upon cooling^[51]. Figure 9 (left) shows examples of fluorescence band sharpening from the Bodipy chromophore.

-Third, these rates appear very fast when considering the quasi-orthogonal dihedral angle

made by the Bodipy plane and the C₆H₄ group (~85°, poor π -conjugation; see Figure 3). This phenomenon has been observed before where two directly bonded porphyrin units forming a quasi-90° dihedral angle still exhibited $k_{\text{ET}}(S_1) = 20 \times 10^{10} \text{ s}^{-1[52]}$.

-Fourth, these rates are also impressive because the low-energy CT absorption band of the azophenine acceptor exhibits no obvious absorptivity in the spectra. Again this observation is supported by DFT computations indicating that f = 0.

For **P2B2Q**, two transient signals are well-resolved. The first one (red trace; Figure 10) exhibits a bleach of the Bodipy absorption band to form the transient signal at 448 nm associated with the Soret band of the porphyrin unit. The second one (blue trace) exhibits two bleach signals (Bodipy and porphyrin) and one transient in the 450-600 nm window due to the porphyrin chromophore. The presence of rise times, here in the order of ~2 ps aand larger than the IRF of the fs TAS set up, expected for energy transfers are evident (Figure 11; red and green traces). From the relaxation time of these transients (2.59 ps = ¹Bodipy*→porphyrin + ¹Bodipy*→Q and 10.0 ps = ¹Porphyrin*→ Q) one can estimate the corresponding $k_{\text{ET}}(S_1)$ from $(1/\tau_{\text{F}}) - (1/\tau_{\text{F}}^\circ)$ where τ_{F} is now replaced by τ_{e} , excited state lifetime of the donor chromophore measured by fs TAS. The data are also in Table 5. The faster $k_{\text{ET}}(S_1)$ values (including the 77 K Streak camera datum) for **P2B2Q** are larger than those for **B2Q** and **B4Q** reflects on additional pathways of energy transfers (Figure 12).



Figure 11. Monitoring the fs TAS of P_2B_2Q showing the ~2 ps rise time (red line).



Figure 12. The various $k_{\text{ET}}(S_1)$ for the polyads at 298 K. Ar = 3,5-(*t*-butyl)₂C₆H₃.

The ¹*Bodipy** \rightarrow *porphyrin process.* It is relevant here to remind that because of the species (*tautomer 1/isomorph 1*) \leftrightarrow (*tautomer 1/isomorph 2*) \leftrightarrow (*tautomer 2/isomorph 1*) \leftrightarrow , most likely with relative population of ~25 %, it is more appropriate to analyse the data in a qualitative manner. Two observations should first be addressed. First, all these rates in the 10¹⁰-10¹¹ s⁻¹ range are considered ultrafast. This is explained by the heavy MO coupling that exhibit the frontier MOs far up the arms with atomic contributions just beside the Bodipy chromophore, and even within the porphyrin unit. This is implying that both a short distance interaction and a through bond energy transfer process taking advantage of the π -conjugation, occur. In addition, the -NH- bridge is a good linker for efficient electronic communication. Second, one can estimate $k_{\text{ET}}(S_1)$ for ¹Bodipy* \rightarrow porphyrin by subtracting, $k_{\text{ET}}(^1\text{Bodipy*}\rightarrow$ porphyrin + ¹Bodipy* \rightarrow **Q**; ~22 x 10¹⁰ s⁻¹)~16 x 10¹⁰ s⁻¹. This methodology was previously applied for other porphyrin-containing triads before and proved beneficial^[53].

For comparison purposes, the choice of these values are based on the fact they were measured on the fs TAS instrument and are for tetra-functionalized azophenines. For a through space energy transfer, this ~16 x 10^{10} s⁻¹ value appears very large and suggests that both processes (*i.e.* Forster (through space)^[54] and Dexter (through bond)^[55]) operate. Finally, **P**₂**B**₂**Q** exhibits some absorptivity at around 675 nm (i.e. $\varepsilon \neq 0$ and the calculated f value for one of the tautomer is not zero as well), so the J-integral is not small, contrarily to that for **B**₂**Q** and **B**₄**Q**. Figure 12 summarizes the $k_{\text{ET}}(S_1)$ at 298 K.

Polyads exhibiting ¹Bodipy* \rightarrow porphyrin processes is well documented^[56-69]. In order to explain this fast rate for ¹Bodipy* \rightarrow porphyrin in **P**₂**B**₂**Q**, comparisons with some literature examples are provided (Figure 13: D1^[70], D2^[71], D3^[72], D4^[73], D5^[73], D6^[74], D7^[74], D8^[74], D9^[75], D10^[76], D11^[76], D12^[76], and D13^[77]. This series can be separated into three subseries: D1-D5 (through space), D6-D9 (through bond), and D10-D13 (directly bonded).

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Figure 13. Representations of various $k_{\text{ET}}(S_1)$ (¹Bodipy* \rightarrow porphyrin) for literature dyads and polyads at 298 K. Ar = 3,5-(*t*-Bu)₂C₆H₄ and Ar' = C₆H₄CHO. Noteworthy, except for **D3**, the presented examples lie among the fastest ones in their category. See the SI for other examples. Moreover, the data for **D8** are from fs TAS at 298 K. The $k_{\text{ET}}(S_1)$'s are 3.4 x 10¹⁰ (77 K) and ~18 x 10¹⁰ s⁻¹ (298 K) based on the Streak camera ^[74].

The former series exhibits no formal conjugation within the bridge between the donor and the acceptor. This is particularly true for **D3**, which exhibit the lowest $k_{\text{ET}}(S_1)$ value (0.003 x 10^{10} s^{-1}). Typically, 0.003 x $10^{10} < k_{\text{ET}}(S_1) < \sim 2.5 \text{ x } 10^{10} \text{ s}^{-1}$ (see the other examples in the SI). The second series exhibits a fully conjugated bridge (notably C₆H₄C=CC₆H₄ and truxene) and the slowest value starts at ~2.5 x 10^{10} s^{-1} (**D6**), then reaches values of (4.5 and

4.7) x 10¹⁰ s⁻¹ for **D8** and **D9**. This systematic increase indicates that a second pathway and mechanism occur (k_{ET} (total) = k_{ET} (Forster) + k_{ET} (Dexter)^[78]). The jump between the structurally similar **D7** and **D8** arises from minor structural modifications. The reason is that these changes induce a variation in the J-integral (k_{ET} (total)). This phenomenon was clearly demonstrated by us recently^[79]. **D8** is very interesting since it exhibits two rates like for **B2Q** and **B4Q**, for the same reason related to the behaviour of the Bodipy donor. Noteworthy, the slower rates could be extracted from both the Streak camera and fs TAS measurements since the τ_e 's are both the same. The faster rate could only be measured by fs TAS. For **P2B2Q**, only fs TAS data are accessible and there is unambiguously only one transient providing a rate for singlet-singlet energy transfer of 38 x 10¹⁰ s⁻¹ for the processes ¹Bodipy*→porphyrin + ¹Bodipy*→Q.

The $k_{\text{ET}}(S_1)$ value for ¹Bodipy* \rightarrow porphyrin (~16 x 10¹⁰ s⁻¹) is, again, very large. With a center-to-center donor-acceptor separations of about ~ 12.2 ± 1.2 Å (see SI for details), and the amplitudes of $k_{\text{ET}}(S_1)$ for the fastest through space (Forster) processes illustrated in Figure 13 (i.e. ~(1 to 2) x 10^{10} s⁻¹), typically Figure 13 shows that $k_{\text{ET}}(S_1)$ increases between 2 to 5 folds going from dvads built upon unconjugated bridge (Forster only; **D1-D5**) vs those using a conjugated linker (Forster + Dexter; **D6-D9**). By taking the fastest rate in the **D1-D5** series for example (Forster; 2.3 x 10^{10} s⁻¹), and multiplying it by 5 folds, then the estimated Dexter contribution is 11.5 x 10^{10} s⁻¹ in $k_{\rm ET}$ (¹Bodipy* \rightarrow porphyrin). Then by applying $k_{\text{ET}}(\text{total}) = k_{\text{ET}}(\text{Forster}) + k_{\text{ET}}(\text{Dexter})$, the resulting value of 13.8 x 10¹⁰ s⁻¹ compares reasonably to the estimated value for P_2B_2O (~16 x 10¹⁰ s⁻¹), and also that for **D8** ($k_{\text{ET}}(S_1) \sim 18 \ge 10^{10} \text{ s}^{-1}$ at 298 K; Streak camera data^[74]). Finally, the series (**D10-D13**) exhibits polyads with directly bonded Bodipy-porphyrin. **D10** to **D12** exhibits rates ranging from (11 to 15) x 10^{10} s⁻¹, which is very similar to that for **P₂B₂O**. The fastest rate in this category is found for **D13** (78 x 10^{10} s⁻¹), with the major structural difference that the zinc(II)porphyrin is replaced by platinum(II)tetrabenzoporphyrin. Table 6 compares polyads with the largest $k_{\rm ET}(S_1)$ values for the ¹Bodipy* \rightarrow porphyrin process, which is useful for the interpretation. Because of the similarity in rates, P_2B_2Q behaves like the directly bonded species and **D8**, a dyad also exhibiting a $C_6H_4C \equiv CC_6H_4$ bridge.

Polyad	fs TAS 298 K	Streak 298 K	Streak 77 K
D8 ^[75]	24 x 10 ¹⁰ , 4.7 x 10 ¹⁰	$\sim 18 \ge 10^{10}$	$3.4 \ge 10^{10}$
P ₂ B ₂ Q ^{this work}	~ 16 x 10 ¹⁰	$> 10 \text{ x } 10^{10 \text{ b}}$	$2.5 \ge 10^{10}$
D11 ^[77]	15 x 10 ¹⁰		
D10 ^[77]	12 x 10 ¹⁰		
D12 ^[77]	11 x 10 ¹⁰		

Table 6. Comparison of the fastest $k_{\text{ET}}(S_1)$'s for ¹Bodipy* \rightarrow porphyrin process (in s⁻¹).^a

^aOnly zinc(II)porphyrin species are indicated for appropriate comparison purposes. ^bThe τ_F value is smaller than the IRF of the Streak camera (~10 ps), thus providing only a lower limit.

The reason arises from the nature of the HOMO and LUMO for *tautomer 1* and *tautomer 2* (Figure 7), for which the atomic contributions of the central azophenine core extend all the way through the arms. So in a Dexter mechanism, the double electron exchange is facilitated. **D8** (which exhibits a fast component of $k_{\text{ET}}(S_1) = 24 \times 10^{10} \text{ s}^{-1}$ and a $k_{\text{ET}}(S_1)$ value of 18 x 10¹⁰ s⁻¹ Streak camera^[74]) also bears a C₆H₄C=CC₆H₄ bridge and also exhibits a fast rate for the same reasons as **P2B2Q**. It appears clear that the ¹Bodipy* \rightarrow porphyrin process occurs via both a through space (minor) and through bond (major) mechanism, a behaviour also known for **D9**^[75], as illustrated in the graphic art.

Data at 77 K are very scarce (see some examples in the SI). By taking the Streak camera $k_{\text{ET}}(S_1)$ data at 77 K (Table 5), the estimated $k_{\text{ET}}({}^1\text{Bodipy}^* \rightarrow \text{porphyrin})$ value for **P_2B_2Q** ((6.3 x 10¹⁰)-(3.8 x 10¹⁰) = 2.5 x 10¹⁰ s⁻¹) falls perfectly (without considering the temperature difference) in the lower range for those of dyads **D6-D9** where $k_{\text{ET}}(\text{total}) = k_{\text{ET}}(\text{Forster}) + k_{\text{ET}}(\text{Dexter})$. It appears that there is a notable decrease in $k_{\text{ET}}(S_1)$ upon cooling, which is not unprecedented. For examples, $k_{\text{ET}}(S_1)$ for **D3** decreases by a factor of ~2 at 77 K, and for **D8** (Streak camera; ~18 x 10¹⁰ (298 K) to 3.4 x 10¹⁰ s⁻¹ (77 K)^[74]), this decrease is ~5 folds. Going from ~16 x 10¹⁰ s⁻¹ (298 K) to 2.5 x 10¹⁰ s⁻¹ (77 K) for **P_2B_2Q**, this decrease is larger (~6-7 folds). The change in J-integral alone cannot explain these large variations (as obvious from a medium change in band-shape in the fluorescence spectra of the Bodipy unit; Figure 9) in **D8** and **P_2B_2Q**. There seems to be, in **P_2B_2Q**, a significant activation barrier drastically changing the outcome of the energy transfer processes. The drastic change in energy transfer behaviour is rare but not unprecedented.

Conclusion

The conclusion of this analysis is that despite some approximations used to rationalize this rather complex antenna system, the firm conclusion is that the ¹Bodipy* \rightarrow porphyrin process in P_2B_2Q proceeds using both Forster and Dexter mechanisms with relative amounts that one cannot exclude the other. At room temperature, the Dexter process is dominant (as illustrated in the graphic art), but at low temperature, it is the other way around most likely due to a large activation barrier. Nonetheless, these rates are undoubtedly in the 10¹⁰ s⁻¹ magnitude. Such rates are particularly impressive in the Dexter regime considering the use of both arms (imine and amine), a particularly long bridge (perhaps the longest so far), and the quasi-right angle formed by the Bodipy and $C_6H_4C \equiv CC_6H_4$ linker planes, to perform the efficient double electron exchange. This conclusion is entirely consistent with the fact that the azophenine radical, when acting as a bridging ligand for various transition metals at the N^N sites, mediates exceptionally strong magnetic exchange coupling constants^[1, 11]. These fast rates also re-inforce the recently made conclusion that the -NH- bridge is prone for efficient electronic communication. It is also interesting to observe the temperature dependence of the $k_{\text{ET}}(S_1)$, more specifically $k_{\rm ET}({\rm total}) = k_{\rm ET}({\rm Forster}) + k_{\rm ET}({\rm Dexter})$. This effect is not surprising when dyads exhibit single bond rotational flexibility^[80]. One down side in this study is the uncertainty caused by the presence of tautomers in solution. This fact is unavoidable if the aim of the research is to characterize the photophysical traits of azophenine. This point bears its importance because it was recently demonstrated that azophenine is a good soluble model to probe the photophysical properties of the far less soluble emeraldine base (*i.e.* polyaniline in its mixed-valence form). In addition, the observation of two distinct fluorescence bands referring to the presence of *tautomer 1* and *tautomer 2* in the singlet excited state is also unique in the literature. The possible ${}^{1}(tautomer \ 1)^{*} \leftrightarrow {}^{1}(tautomer \ 2)^{*}$ interconversion should occur in the ps time scale, similar to what was recently reported for corrole^[81]. To achieve the evaluation of the rate for interconversion by time-resolved fluorescence spectroscopy, a laser system with a shorter IRF response (~1 ps, not 10 ps) is required. However, the most important conclusion of this work is that the notoriously nonluminescent uncycled azophenine is not "photophysically" inert. To the contrary. Its contribution to the antenna processes for both mediation of the double electron exchange and acting as an energy acceptor (despite f = 0 for two cases) is phenomenal. Current investigation of using BF_2^+ units at the N^N sites in order to cycle azophenine derivatives are underway. The aim is to rigidify the center core of this star molecule and observe the effect of the resulting photophysical properties and its applicability for the design of photonic materials, but also to remove the possibility of tautomerization processes, if not desired.

Experimental Section

Materials. Compound $4^{[16]}$, $5^{[82]}$, $6^{[15]}$, $8^{[41]}$ were prepared according to literature procedures. PdCl₂(PBu₃)₂, CuI, Pd(dba)₃, Ph₃As, ethynylbenzene, Zn(AcO)₂ were purchased from Aldrich and were used as received. All flasks were dried under a flame to eliminate moisture. Solvents were distilled from appropriate drying agents and other reagents were used as received.

Instruments. The ¹H and ¹³C NMR spectra were collected on a Bruker DRX400 spectrometer using the solvent as chemical shift standard. The coupling constant are in Hz. MALDI-TOF mass spectra were recorded on a Bruker BIFLEX III TOF mass spectrometer (Bruker Daltonics, Billerica, MA, USA) using a 337 nm nitrogen laser with dithranol as matrix. The spectra were measured from freshly prepared samples. The absorption spectra in the solution (typical concentrations were in the range of 10^{-5} M to 10^{-6} M) were measured on a Varian Cary 300 Bio UV-vis spectrometer at 298 K and on a Hewlett-Packard 8452A diode array spectrometer with a 0.1 s integration time at 77 K. The steady state fluorescence (< 820 nm; typical concentrations were in the range of 0.5 x 10^{-5} to 0.5 x 10^{-6} M) and the corresponding excitation spectra were acquired on an Edinburgh Instruments FLS980 phosphorimeter equipped with single monochromators. Fluorescence lifetime measurements were made with the FLS908 spectrometer using a 378 nm picosecond pulsed diode laser (fwhm = 78 ps) as an excitation source. Data collection on the FLS980 system was performed by time correlated single photon counting (TCSPC). All fluorescence spectra were corrected for instrument response. For these measurements, the typical concentrations were in the range of 1×10^{-5} to 1×10^{-6} M.

Fast kinetic fluorescence measurements. The short components of the fluorescence decays were measured using a Streak camera (Axis-TRS, Axis Photonique Inc.) with less

than 8 ps resolution where the excitation wavelength, λ_{exc} , was set using the second harmonic generation (SHG) of a Soltice (SpectraPhysics) Ti-sapphire laser ($\lambda_{exc} = 500$ nm; FWHW ≈ 100 fs; pulse energy = 3.5 mJ per pulse, rep. rate = 1 kHz; spot size $\approx 400 \ \mu$ m). The time constants associated with the decay curves in both Streak Camera were extracted by global analysis of the corresponding fluorescence decay curves using the Glotaran (http://glotaran.org) analysis program permitting to extract a sum of independent exponentials ($I(\lambda, t) = C_1(\lambda) \times e^{-\frac{t_1}{\tau}} + C_2(\lambda) \times e^{-\frac{t_2}{\tau}} + \cdots$).

Femtosecond transient absorption measurements. The fs transient spectra and decay profiles were acquired on a homemade system using a Soltice/OPA-800CF (Spectra Physics) Ti-sapphire laser (λ_{ex} - 500 nm; FWHM - 120 fs; pulse energy - 3.5 mJ per pulse, max rep. rate - 1 MHz, spot size - 200 µm) a white light continuum generated inside a sapphire window and custom-made dual CCD camera 64 × 1024 pixels sensitive between 200 and 1100 mn (S7030, Spectronic Devices). The results were also globally analysed with the program Glotaran (http://glotaran.org) permitting to extract a sum of independent exponentials ($I(\lambda, t) = C_1(\lambda) \times e^{-\frac{t_1}{\tau}} + C_2(\lambda) \times e^{-\frac{t_2}{\tau}} + \cdots$).

Computations. All density functional theory (DFT) calculations were performed with Gaussian 09^[83] at the Université de Sherbrooke with the Mammouth supercomputer supported by Le Réseau Québécois De Calculs Hautes Performances. The DFT geometry optimisations and time dependant DFT (TD-DFT) calculations^[84-93] were carried out using the B3LYP method. A 6-31g* basis set was used for C, H, N atoms^[94-99]. Theoretical UV-visible absorption spectra were obtained using GaussSum^[100].

Synthesis of B₂Q. To a 50 mL Schlenk tube was added 20 mL of THF. The solvents were purged with argon before addition of 5 (352 mg, 0.7 mmol), compound 6 (158 mg, 0.23 mmol), Pd(dba)₂ (2.6 mg, 2.8×10^{-3} mmol), Et₃N (1 mL). The resulting solution was stirred at RT. After complete conversion of the starting materials as monitored by TLC, the solvent was evaporated. The product was purified on a silica column (Hexanes/CHCl₃=3/1 as the solvent) to give the target compound **B**₂Q as red solid. (200 mg, 60%). ¹H NMR (300 MHz, CDCl₃) δ 8.45 (s, 2H), 7.70 (d, *J* = 8.1 Hz, 4H), 7.59 (d, *J* = 8.3 Hz, 4H), 7.49 (d, *J* = 8.3 Hz, 4H), 7.32 (d, *J* = 8.2 Hz, 5H), 7.18 – 6.96 (m, 8H), 6.36 (s, 2H), 2.57 (s, 12H), 2.34 (q,

J = 7.6 Hz, 8H), 1.37 (s, 12H), 1.02 (t, *J* = 7.5 Hz, 12H), 0.28 (s, 18H). ¹³C NMR (76 MHz, CDCl₃) δ 154.01, 139.32, 138.25, 135.76, 133.12, 132.94, 132.75, 132.19, 130.57, 128.53, 123.92, 121.11, 120.76, 104.90, 92.36, 90.62, 88.99, 29.72, 17.10, 14.63, 12.55, 11.91, 0.02. MALDI-TOF: m/z calculated C₉₀H₉₀B₂F₄N₈Si₂ 1437.55, found 1419.96 (M-F).

Synthesis of 7. To a 100 mL round bottom flask was added 20 mL of DCM/MeOH (v/v = 2:1). The solvents were purged with argon before addition of **B**₂**Q** (80 mg, 0.06 mmol). K₂CO₃ (4 mL, 4 mmol) was then added. The reaction was stirred for 2 hours prior to filter off the salt under vacuum. Chromatography on silica gel afforded the target compound as red solid (67 mg, 92%). ¹H NMR (300 MHz, CDCl₃) δ 8.42 (s, 2H), 7.70 (d, *J* = 8.1 Hz, 4H), 7.55 (dd, *J* = 16.8, 8.3 Hz, 8H), 7.34 (s, 3H), 7.31 (s, 2H), 7.07 (t, *J* = 8.6 Hz, 8H), 6.36 (s, 2H), 3.12 (s, 2H), 2.57 (s, 12H), 2.34 (q, *J* = 7.4 Hz, 8H), 1.37 (s, 11H), 1.02 (t, *J* = 7.5 Hz, 12H). MALDI-TOF: m/z calculated C₈₄H₇₄B₂F₄N₈ 1293.19, found 1275.93 (M-F+H).

Synthesis of 9. Compound **8** (358 mg, 0.40 mmol) and Zn(AcO)₂ (110 mg, 0.60 mmol) were dissolved in 30 mL of mixture of DCM/MeOH (v/v = 2:1), the reaction was stirred at room temperature. After complete conversion of the starting materials as monitored by TLC, the solvent was evaporated. Chromatography on silica gel afforded the target compound as red solid. Yield: 364 mg (95 %). ¹H NMR (300 MHz, CDCl₃) δ 9.85 (d, *J* = 4.8 Hz, 2H), 9.05 (d, *J* = 4.8 Hz, 2H), 8.95 (dd, *J* = 11.4, 4.7 Hz, 4H), 8.21 (dd, *J* = 7.6, 1.7 Hz, 2H), 8.09 (d, *J* = 1.8 Hz, 4H), 7.84 (t, *J* = 1.8 Hz, 2H), 7.77 (dd, *J* = 7.2, 5.4 Hz, 3H), 1.56 (s, 37H). ¹³C NMR (76 MHz, CDCl₃) δ 152.06, 151.55, 150.83, 150.49, 148.67, 142.62, 141.38, 137.64, 134.21, 133.90, 132.59, 132.30, 129.78, 127.59, 126.57, 123.32, 122.00, 121.01, 80.75, 35.07, 31.76. MALDI-TOF: m/z calculated C₅₄H₅₅IN₄Zn, 950.28, found 951.25 (M+H).

Synthesis of P₂B₂Q. To a 50 mL Schlenk tube was added 20 mL of THF. The solvents were purged with argon before addition of compound 7 (40 mg, 0.03 mmol), compound 9 (118 mg, 0.12 mmol), Pd(dba)₂ (2.6 mg, 2.8×10^{-3} mmol), Et₃N (1 mL). The resulting solution was stirred at RT. After complete conversion of the starting materials as monitored by TLC, the solvent was evaporated. The product was purified on a silica column (Hexanes/CHCl₃=3/1 as the solvent) to give the target compound P₂B₂Q as claybank solid.

(47 mg, 52%). ¹H NMR (300 MHz, CDCl₃) δ 9.91 (d, *J* = 4.6 Hz, 4H), 9.09 (d, *J* = 4.7 Hz, 4H), 8.93 (d, *J* = 4.7 Hz, 4H), 8.88 (d, *J* = 4.7 Hz, 4H), 8.70 – 8.56 (m, 2H), 8.19 (dd, *J* = 6.4, 2.3 Hz, 4H), 8.09 (d, *J* = 1.7 Hz, 9H), 7.82 (t, *J* = 1.8 Hz, 5H), 7.74 (d, *J* = 6.5 Hz, 8H), 7.62 (d, *J* = 6.8 Hz, 5H), 7.52 (d, *J* = 8.0 Hz, 5H), 7.24 – 7.15 (m, 2H), 7.09 (d, *J* = 8.1 Hz, 3H), 6.61 (s, 2H), 2.44 (s, 12H), 2.11 (dd, *J* = 15.4, 6.6 Hz, 8H), 1.12 (s, 12H), 0.79 (t, *J* = 9.6 Hz, 14H). ¹³C NMR (76 MHz, CDCl₃) δ 153.84, 152.19, 150.85, 150.15, 150.05, 148.74, 142.66, 141.40, 139.16, 138.07, 135.51, 134.21, 133.20, 132.82, 132.75, 132.62, 132.60, 132.27, 132.15, 132.03, 129.84, 128.34, 126.59, 123.55, 120.95, 77.44, 77.22, 77.01, 76.59, 35.08, 31.76, 29.71, 16.92, 14.48, 14.13, 12.45, 11.73, 1.04. MALDI-TOF: m/z calculated C₁₉₂H₁₈₂B₂F₄N₁₆Zn₂, 2942.05, found 2942.86 (M+H) and 2922.89 (M-F+H).

Synthesis of Por. To a 50 mL Schlenk tube was added 20 mL of THF, the solvents were purged with argon before addition of PdCl₂(PBu₃)₂ (1.2 mg, 1.9 mmol), CuI (33 mg, 0.17 mmol), Et₃N (3mL), and compound **9** (100 mg, 0.11mmol), phenylacetylene (34 µl, 0.315 mmol). The resulting solution was stirred at room temperature for 8h. After complete conversion of the starting materials as monitored by TLC, the solvent was evaporated. Chromatography on silica gel afforded the target compound as green solid. (80 mg, 82%). ¹H NMR (300 MHz, CD₂Cl₂) δ 9.93 (d, *J* = 4.7 Hz, 2H), 9.12 (d, *J* = 4.7 Hz, 2H), 8.97 (d, *J* = 4.7 Hz, 2H), 8.91 (d, *J* = 4.7 Hz, 2H), 8.23 (dd, *J* = 7.4, 1.9 Hz, 2H), 8.14 (d, *J* = 1.9 Hz, 4H), 8.13 (s, 1H), 8.10 (d, *J* = 1.2 Hz, 1H), 7.90 (t, *J* = 1.8 Hz, 2H), 7.80 (q, *J* = 5.2 Hz, 3H), 7.64 (dd, *J* = 8.0, 6.5 Hz, 2H), 7.56 (dd, *J* = 10.3, 4.4 Hz, 1H), 1.59 (s, 37H). ¹³C NMR (76 MHz, CD₂Cl₂) δ 134.24, 133.15, 132.14, 132.02, 131.53, 130.55, 129.77, 128.73, 127.57, 126.56, 123.47, 121.16, 34.95, 31.45. MALDI-TOF: m/z calculated C₆₂H₆₀N₄Zn, 924.41, found 925.41 (M+H).

Synthesis of B₄Q. To a 50 mL Schlenk tube was added 20 mL of THF. The solvents were purged with argon before addition of 5 (210 mg, 0.42 mmol), compound 4 (37 mg, 0.07 mmol), Pd(dba)₂ (2.6 mg, 2.8×10^{-3} mmol), Et₃N (1 mL). The resulting solution was stirred at RT. After complete conversion of the starting materials as monitored by TLC, the solvent was evaporated. The product was purified on a silica column (Hexanes/CHCl₃=3/1 as the solvent) to give the target compound **B**₄Q as red solid. (70 mg, 50%). ¹H NMR (300 MHz, CDCl₃) δ 8.47 (s, 2H), 7.69 (d, *J* = 8.1 Hz, 8H), 7.60 (d, *J* = 8.2 Hz, 8H), 7.31 (d, *J* = 8.2 Hz, 9H), 7.12 (d, *J* = 8.0 Hz, 8H), 6.44 (s, 2H), 2.55 (s, 24H), 2.31 (dd, *J* = 14.8, 7.2 Hz, 9H), 7.2 Hz, 8H

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18H), 1.35 (s, 19H), 0.99 (t, J = 7.5 Hz, 25H). ¹³C NMR (76 MHz, CDCl₃) δ 154.06, 139.20, 138.13, 135.81, 132.94, 132.77, 132.15, 130.54, 128.56, 123.88, 120.85, 90.62, 88.88, 45.81, 17.08, 14.61, 12.55, 11.89. MALDI-TOF: m/z calculated C₁₃₀H₁₂₄B₄F₈N₁₂, 2049.03, found 2050.05 (M+H).

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Table of content



Graphic art

Two Bodipy and zinc(II)porphyrin antennas were connected to an uncycled azophenine, which became fluorescent in the near-IR region and mediated two unexpectedly ultrafast S_1 energy transfers: ¹Bodipy* $\rightarrow \mathbf{Q}$ ($k_{\text{ET}} = 10^{10} \cdot 10^{11} \text{ s}^{-1}$) and ¹Bodipy* \rightarrow porphyrin ($k_{\text{ET}} \sim 16 \times 10^{10} \text{ s}^{-1}$), due to the rather low absorptivity properties of the lowest energy charge transfer excited state of azophenine. The Dexter mechanism is the dominent process.