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Efficient supramolecular synthesis of a robust circular light-harvesting Bodipy-dye based array†

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We herein present the supramolecular construction of a completely fluorescent unquenched multichromophoric wheel consisting of boron dipyrromethene dyes arranged perpendicularly to the circular plane.

Understanding and mimicking nature's thinking in creating well-defined cyclic light-harvesting chromophoric scaffolds for capturing and temporarily storing sunlight energy remains a formidable task.¹ To this end, a promising route would be the construction – via self assembly of suitable chromophoric building blocks – of rigid and robust cyclic frameworks promoting fixed separation and orientation of dyes so that the highly concentrated chromophoric “ensemble” to be free of excitation energy sinks.

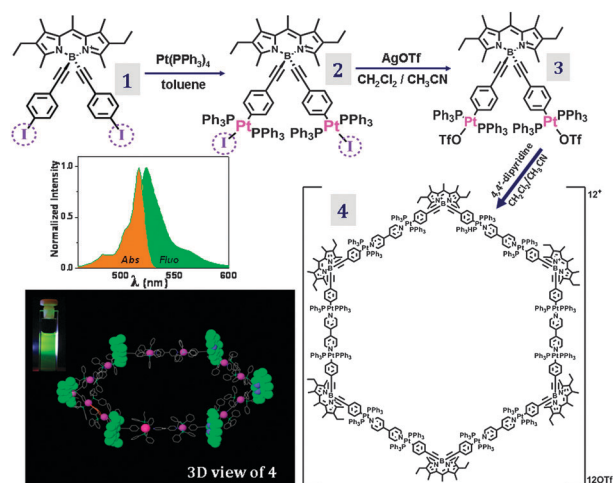
Dendrimeric structures² and discrete cyclic porphyrin arrays³ are the most highlighted approach paths. While significant developments have been made in the construction of these chromophoric arrays, well-defined structure–function correlations still lack sufficient awareness. The covalent bonding nature of the linked chromophores in these systems in conjunction with their conformational looseness lead to non-radiative channels making them less suitable for saving temporarily the incident light energy.

Precise donor–acceptor supramolecular synthesis and in particular coordination-driven self-assembly provide a sophisticated and time-saving way to construct compact and stiff metallosupramolecular architectures with well-defined shape and size not accessible by traditional synthesis.⁴ However, as far as the fabrication of light-harvesting assemblies is concerned, nearly all of them suffer from the same drawback—fast dissipation loss of the excitation energy upon binding of the electron rich donor to the heavy metal cation of the acceptor.⁵ While some developments have been made towards protecting the emissive state of a perylene⁶ and of a Bodipy⁷ based donor (pyridine dye), there are no advances yet for allowing the manifestation of tailor-made, strongly emissive acceptors

(dye-M^{+x}) capable of programming precise supramolecular synthesis of functional photonic materials.

We present herein a unique, brightly fluorescent acceptor of the popular Bodipy laser dyes⁸ (**3**; Scheme 1) in which the heavy metal cation (Pt⁺) is directly attached to the backbone of the chromophoric building-block using appropriate rigid –C≡C–Ph–Pt⁺ arms that synthetically replace the fluorine atoms of the sp³ hybridized boron of the basic Bodipy unit. This connectivity appears to be the key for saving light as it enables efficient disconnection and protection of the π electronic backbone of the Bodipy from loss of the excitation energy into quenching sites induced by the heavy metal^{7,9} (e.g., charge-transfer states and heavy atom effect). The crystal structure† of the tailor-made starting chromophoric tecton **2** (precursor of **3**) formed by reaction of the Bodipy unit¹⁰ **1** with Pt(PPh₃)₄ and the design rationale of the subsequent construction of a shape-persistent, completely fluorescent unquenched multichromophoric wheel are shown, respectively, in Fig. 1 and Scheme 1. Indeed, as mentioned above, in spite of the presence of two pairs of heavy atoms covalently bound to **2** i.e., platinum (Pt) and iodine(I) – the latter also known as ‘killer’ of fluorescence – the emitting state of **2** is not affected at all i.e., Φ = 0.87; τ_f = 6.33 ns (see Table 1).

The above crystal structure reveals features that appear to be decisive for the size, shape and excited state of the final



Scheme 1 Schematic illustration of the synthesis of a unique hexagonal light-harvesting multichromophoric unit composed of Bodipys.

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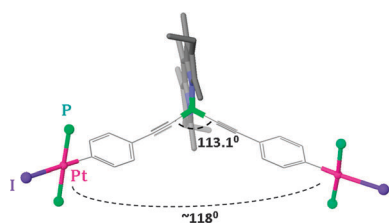


Fig. 1 Crystal structure of tecton **2**; the phosphine phenyl groups and hydrogen atoms are omitted for clarity. Carbon: grey; boron: green; nitrogen: blue light.

Table 1 Photophysical data for the Bodipy derivatives (**1**, **2** and **3**) and the assembly (**4**) in CHCl_3 at 23 °C

	λ_{abs}^a ($\text{e}/\text{M}^{-1} \text{cm}^{-1}$) ^b	λ_{fluor}^c	Φ_f^d	τ_f^e (ns)	k_f (k_{nr}^f) (10^8 s^{-1})	$r_{(0)}^g$
1	516 (78 100)	533	0.86	6.17	1.39 (0.23)	0.37
2	517 (77 800)	534	0.87	6.33	1.37 (0.21)	0.37
3	516 (77 300)	533	0.86	6.10	1.41 (0.23)	0.37
4	517 (77 900)	533	0.88	6.34	1.39 (0.19)	0.36

^a Absorption maximum. ^b Extinction coefficient per dye unit. ^c Fluorescence maximum. ^d Fluorescence quantum yield. ^e Fluorescence lifetime. ^f Radiative (k_f) and non-radiative (k_{nr}) rate constants. ^g Limited fluorescence anisotropy (± 0.005) obtained in 2-MeTHF at 93 K.

assembly (Fig. 1). Steric bulkiness between the aromatic hydrogen of the phosphine groups and the side methyl groups of the Bodipy subunit results in (a) a noticeable deviation of the sp^3 hybridized boron-arms angle (113.1°) relative to the normal tetrahedral one (109.5°) and (b) a systematic bending distributed across all the angular parts of the $-\text{C}\equiv\text{C}-\text{Ph}-\text{Pt}-\text{I}$ arm. The above have a profound effect on the highly stereodirectional bonding angle $\text{Pt}-\text{B}-\text{Pt}$ ($\sim 118^\circ$) which approximately approaches 120° needed for a regular hexagonal assembly.^{4b}

Evidence of the formation of the assembled entity **4** in solution is provided by ^{31}P , ^1H , ^{13}C NMR analysis, 2D diffusion-ordered NMR (DOSY), 2D rotating frame nuclear Overhauser effect spectroscopy (ROESY), electrospray ionization mass spectrometry (ESI-MS) and fluorescence spectroscopy methods both steady-state and time-resolved. The self-organization of **4** in the solid state was also investigated with Scanning Tunneling Microscopy (STM).

$^{31}\text{P}\{^1\text{H}\}$ NMR analysis of **4** in CDCl_3 is consistent with the formation of a single, highly symmetrical species by the appearance of an extremely sharp singlet at 21.55 ppm (Fig. 2). The upfield shift ($\Delta\delta = 0.98$ ppm) relative to the platinum acceptor **3** along with the change of the flanking ^{195}Pt satellites ($\Delta^1 J_{\text{PPt}} = 3027$ Hz) further suggests coordination of platinum centers of **5** with the pyridine donor (Fig. S2, ESI[†]). Examination of the ^1H NMR spectrum provides clear indications of the presence of a highly symmetrical supramolecular entity. The signals of the α and β hydrogen nuclei of the pyridine ring are sharp and significantly upfield shifted by 0.67 and 0.50 ppm, respectively, demonstrating a strongly perturbed magnetic field in the complexed state (see Fig. 2; inset). The above contacts are further manifested by the observation of crossed peaks in the ROESY spectrum between the α proton of the pyridine and those of the phosphine phenyl rings (Fig. S3, ESI[†]). No disintegration of the assembly was observed upon dilution up to $\sim 3 \times 10^{-6}$ M. Good thermodynamic stability of **4** was found in CH_2Cl_2 , CHCl_3 , THF and acetone. Peaks attributed to the consecutive loss of triflate counterions from a [6 + 6] hexagonal macrocycle

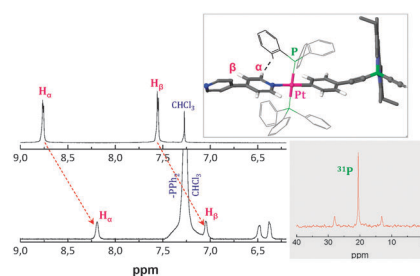


Fig. 2 ^1H NMR spectra of the donor 4,4' bipyridine (1.0 mM 500 MHz, 298 K, CDCl_3) and upon coordination (down) with the acceptor **3**. Insets: (top); connection topology between donor-acceptor; (down) $^{31}\text{P}\{^1\text{H}\}$ (121.4 MHz, 298 K, CDCl_3) of **4**.

($[\text{M} - 5\text{OTf}]^{5+}$, $m/z = 2699.71$; $[\text{M} - 7\text{OTf}]^{7+}$, $m/z = 1885.67$; $[\text{M} - 4\text{OTf}]^{4+}$, $m/z = 3412.11$ and $[\text{M} - 8\text{OTf}]^{8+}$; $m/z = 1631.34$) were observed by electrospray mass spectrometry in acetone. Experimental isotopic partners centered at these m/z values were found to be in excellent agreement with their theoretical isotopic distribution (Fig. S4–S7, ESI[†]).

The 2D DOSY spectrum provides a signature for the presence of a distinct supramolecular identity. Fig. 3 compares (in CDCl_3 at 298 K) the *translational* diffusion coefficient (D) of the assembled entity **4** with that of the precursory building block **2** for which the molecular dimensions are precisely defined by the available crystal structure.

For **2** alone (1.0 mM) a D of $(5.08 \pm 0.10) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ was measured corresponding to an experimental hydrodynamic diameter of 15.8 Å. This value is very close to that predicted (14.5 Å) regarding **2** as a perfect sphere. The DOSY spectrum of the supramolecular entity **4** (1.0 mM) reveals a single band manifesting that all linked subunits (*i.e.*, donors and acceptors) are diffused together. The measured $D = (8.43 \pm 0.13) \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ is just 6-fold smaller than that of the building block **2**. This gives an experimental hydrodynamic diameter of ~ 9.5 nm which, albeit it cannot be corresponded strictly to a perfect sphere as the Stokes–Einstein equation postulates,¹¹ is roughly in agreement with predictions based on models for the hexagonal entity.

Further information on the size and the absence of aggregation of the assembled entity was obtained by estimating the *rotational* correlation time (θ) in CHCl_3 at 23 °C, using the time-resolved fluorescence depolarization method¹¹ (Fig. S8, ESI[†]). The rotational correlation time for the supramolecular assembly **4**

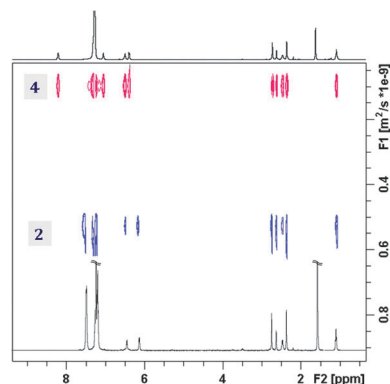


Fig. 3 DOSY spectra: building block **2** (bottom) and supramolecular entity **4** (top) in CDCl_3 at 298 K.

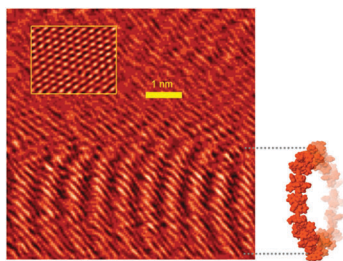


Fig. 4 STM image of **4** self-organized on highly ordered pyrolytic graphite (HOPG). The field size is 7 nm × 7 nm. The hexagonal unit (right) was obtained by modelling.

was determined to be $\theta = 1.32 \pm 0.05$ ns which is approximately 6.5 times higher than that of **2** ($\theta = 0.21 \pm 0.01$ ns). The former experimental value corresponds to a rotating entity with $V_{\text{mol}} \approx 10.500 \text{ \AA}^3$ which is highly consistent with that of **4** calculated by modeling ($\sim 10.000 \text{ \AA}^3$) suggesting that the hexagonal assembly rotates as a single entity.

Conformational rigidity and chromophoric dipole orientation are crucial as far as the construction of an efficient light-harvesting unit is concerned.¹ Clearly, the *fixed separation* and *orientation* of the closely positioned chromophores allow both concentration quenching obviation and energy transfer optimization between strongly-coupled adjacent dipoles. Our attempts to crystallize the hexagonal suprastructure **4** have failed so far. However, the fact that (a) the absorption–emission (S_0 – S_1) electronic transition dipoles of the Bodipy chromophore are polarized along its long molecular axis¹² and (b) the fluorescence decays are mono-exponential (Fig. S9, ESI†) allow obtaining – by means of fluorescence polarization spectroscopy – precise structural information not accessible by other powerful characterization techniques such as NMR spectroscopy. The high degree of orientation of the chromophoric dipoles in **4** was demonstrated by measuring the fluorescence anisotropy r in a frozen 2-methyltetrahydrofuran (2-MeTHF) solution of **4** wherein depolarization by molecular tumbling has ceased. The fluorescence anisotropy r reaches the value of 0.36 ± 0.05 which is very close to the limited value $r_0 = 0.37 \pm 0.05$ of the isolated Bodipy subunit.⁷ We note that r is highly sensitive to the mutual orientation of the adjacent coupled dipoles (e.g., propagation of the excitation through randomly oriented nearest neighbor dipoles would cause nearly full depolarization, as it is well known that when excitation undergoes a random walk among i identical acceptors the magnitude of r should be equal¹³ to r_0/i i.e., ~ 0.06 for $i = 6$ herein). Our findings are interpreted as evidence of electronic excitation energy transfer – *via* resonance interactions (Förster mechanism, FRET) – between nearly parallel neighboring chromophores,¹⁴

$$k_{\text{eet}} = 3/2(\kappa^2/\tau_f)(R_0/R)^6 \quad (1)$$

The mutual parallelism of the Bodipy dyes in **4** results in an orientation factor $\kappa^2 \approx 1$ which, when combined with (i) the center-to-center interchromophoric distance $R \approx 16 \text{ \AA}$, (ii) the extremely large critical Förster distance for Bodipys⁹ $R_0 \approx 57 \text{ \AA}$ and (iii) the fluorescence lifetime of **4** ($\tau_f = 6.34$ ns), demonstrates a high rate constant $k_{\text{eet}} = 4.8 \times 10^{11} \text{ s}^{-1}$ for energy hopping between nearest-neighbor chromophores (see eqn (1)).

The above rate constant, which is over ~ 3000 times larger than the *intrinsic* deactivation rate of the excited-state of the Bodipy subunit ($k_{\text{int}} = 1/\tau_f = 1.58 \times 10^8 \text{ s}^{-1}$), suggests that the excitation energy is efficiently spread and temporarily stored (during the lifetime of the excited state) among the cyclically arranged chromophores.

The solid state self-organization of the cyclic supra-molecular structure (**4**) was investigated by scanning tunnelling microscopy (STM). By applying a 10 μl droplet of a $\sim 10^{-5}$ M solution of **4** in CHCl_3 onto the basal plane of freshly cleaved HOPG, the images showed that the circular supra-molecular units form tubular assemblies along the surface plane (Fig. 4).

In summary, herein we present the one-step supramolecular synthesis of a light-harvesting and brightly fluorescent hexagonal assembly in which the chromophoric building blocks are subjected to precise topological control. This approach can open a new space for solar harvesting and photonics research.¹⁵

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Notes and references

- G. D. Scholes, G. R. Fleming, A. Olaya-Castro and R. van Grondelle, *Nat. Chem.*, 2011, **3**, 763–774.
- (a) S.-C. Lo and P. L. Burn, *Chem. Rev.*, 2007, **107**, 1097–1116; (b) J. Iehl, J.-F. O. Nierengarten, A. Harriman, T. Bura and R. Ziessel, *J. Am. Chem. Soc.*, 2012, **134**, 988–998.
- (a) N. Aratani, D. Kim and A. Osuka, *Acc. Chem. Res.*, 2009, **42**, 1922–1934; (b) M. C. O’Sullivan, J. K. Sprafke, D. V. Kondratuk, C. Rinfray, T. D. W. Claridge, A. Saywell, M. O. Blunt, J. N. O’Shea, P. H. Beton, M. Malfois and H. L. Anderson, *Nature*, 2011, **469**, 72–75.
- (a) P. Jin, S. J. Dalgarno and J. L. Atwood, *Coord. Chem. Rev.*, 2010, **254**, 1760–1768; (b) R. Chakrabarty, P. S. Mukherjee and P. J. Stang, *Chem. Rev.*, 2011, **111**, 6810–6918.
- I. Beletskaya, V. S. Tyurin, A. Y. Tsivadze, R. Guillard and C. Stern, *Chem. Rev.*, 2009, **109**, 1659–1713.
- A. Sautter, B. K. Kaletas, D. G. Schmid, R. Dobrawa, M. Zimine, G. Jung, I. H. M. van Stokkum, L. De Cola, R. M. Williams and F. Wurthner, *J. Am. Chem. Soc.*, 2005, **127**, 6719–6729.
- A. Kaloudi-Chantzea, N. Karakostas, C. P. Raptopoulou, V. Psycharis, E. Saridakis, J. Griebel, R. Hermann and G. Pistolis, *J. Am. Chem. Soc.*, 2010, **132**, 16327–16329.
- A. Loudet and K. Burgess, *Chem. Rev.*, 2007, **107**, 4891–4932.
- A. Barbieria, B. Ventura and R. Ziessel, *Coord. Chem. Rev.*, 2012, **256**, 1732–1741.
- A. Harriman, L. Mallon and R. Ziessel, *Chem.–Eur. J.*, 2008, **14**, 11461–11473.
- J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Kluwer Academic/Plenum Publishers, New York, 2nd edn, 1999.
- J. Karolin, L. B. A. Johansson, L. Strandberg and T. Ny, *J. Am. Chem. Soc.*, 1994, **116**, 7801–7806.
- G. Pistolis, A. K. Andreopoulou, A. Malliaris and J. K. Kallitsis, *J. Phys. Chem. B*, 2005, **109**, 11538–11543.
- FRET between identical adjacent dyes cannot be detected straightforwardly - for they have indistinguishable absorption and emission spectra preventing thus the observation of a rising component in a time resolved experiment (TRE). Preliminary results from our lab on the construction of a macrocycle *via* the combination of a pair of Bodipys (a Bodipy1-donor and a Bodipy2-acceptor that spectrally differ slightly) straightforwardly manifest complete ($\sim 100\%$) electronic energy transfer from the donor to the acceptor.
- (a) I. B. Martini, I. M. Craig, W. C. Molenkamp, H. Miyata, S. H. Tolbert and B. J. Schwartz, *Nat. Nano*, 2007, **2**, 647–652; (b) T. N. Singh-Rachford and F. N. Castellano, *Coord. Chem. Rev.*, 2010, **254**, 2560–2573.