"Efficient Supramolecular Synthesis of a Robust Circular Light – Harvesting Bodipy-dye Based Array"

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Experimental details

Materials

Solvents were purified as follows. CH_2Cl_2 and CH_3CN were purified according to literature procedures¹ and were distilled over CaH_2 . Diethyl ether and THF were purified according to literature procedures¹ and were distilled over Na / benzophenone. $CDCl_3$ was used without further purification. All solvents were freeze-thaw-pump degassed three times before use. All commercial reagents were ACS reagent grade and were obtained as follows: 2,4-dimethyl-3-ethylpyrrole (Aldrich), acetyl chloride (Fluca), boron trifluoride diethyl etherate (Aldrich), triethylamine (Aldrich), (4-iodophenylethynyl)trimethylsilane (Aldrich) tetrakis(triphenylphosphine)platinum(0) (Acros Organics) and silver trifluoromethanesulfonate (Acros Organics), and they were all used as received; 4,4-bis-(4-iodophenylethynyl)-1,3,5,7,8-pentamethyl-2,6-diethyl-3a,4a-diaza-sindacene was prepared according to similar literature procedures.²

Instrumentation and Methods

Syntheses of 2, 3 and 4 were conducted under a dry argon atmosphere using Schlenk techniques. ¹H NMR spectra were recorded on a Bruker Avance DRX 500 spectrometer at 500 MHz and 25 °C and all chemical shifts are reported in ppm relative to the proton resonance resulting from incomplete deuteration of the NMR solvent: CDC1₃ (7.26 ppm). ¹³C NMR spectra were recorded on a Bruker Avance DRX 250 spectrometer at 62.9 MHz and 25 °C, and all chemical shifts are reported in ppm relative to the carbon resonance of the deuterated NMR solvent: CDC1₃ (77.0 ppm). ³¹P NMR spectra were recorded a Bruker Avance DRX 500 spectrometer at 202.46 MHz and 25 °C, and all chemical shifts are reported in ppm relative to external 85% H₃P0₄ at 0.00 ppm. 2D ROESY spectra were acquired using a mixing time of 400 ms. DOSY NMR experiments were carried out as follows: solutions of 4 cm height were used to ensure gradient linearity along the samples. The temperature was controlled using a 135 L/min air flow and kept at 298.0 \pm 0.1 K. The measured 90 degree pulses were 9.78 µs for 4 and 9.63 µs for 2. A delay $d1 = 4*T_1$ (measured $T_1 = 1.45$ s for 2 and 2.00 s for 4) was used for the measurements, which were carried out with the gradient spin echo sequence ledbpgs2s1d. Data were acquired with 32 or 16 scans for each gradient step, 4 dummy scans, a 2.8 ms (for 2) and 4 ms (for 4) gradient pulse (δ), a linear gradient of 16-32 steps between 2% and 95% and diffusion time (Δ) 100 ms. Processing was carried out with Bruker's Topspin 2.1 software. Absorption spectra were recorded on a Perkin-Elmer Lambda-16 spectrophotometer. Steady-state fluorescence spectra were accomplished by the Perkin-Elmer model LS-50B Edinburgh Instruments and the model FS-900

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spectrofluorometer. Fluorescence lifetimes (τ) were determined using the time correlated single-photon counter FL900, of the above Edinburgh Instruments setup. Fluorescence quantum yield measurements of the compounds **1**, **2**, **3**, **4** in dichloromethane ($\eta_{(CH2CI2)} = 1.424$) were obtained relative to Rhodamine 6G in ethanol (Φ =0.88, $\eta_{(EtOH)} = 1.358$).

STM measurements were performed with an NT-MDT Solver Pro 45 Scanning Tunneling Microsope using a Pt/Ir wire tip. High resolution images were obtained using the Constant Height mode with a probe current of 120pA and a biasing voltage of 200mV. In the case of small size fields (<20nm), the feedback signal was set to OFF and the maximum scanning frequency of 62.5Hz was used. The STM signal of the molecule is superimposed to the one coming from the carbon substrate. The inset in Figure 4 (manuscript) shows the reference HOPG substrate at the same dimensions. The exposed arc of the stacked molecules has a length of 4-5 nm while the distance between the rings is ~ 0.8nm.

Syntheses of 2, 3, 4

Synthesis of 2 A 50 mL round-bottom Schlenk flask was loaded with 55 mg (0.075 mmol) of 1 which were dissolved in 7 mL of toluene and 208 mg of Pt(PPh₃)₄ (0.167 mmol) were subsequently added. The mixture was heated at 80 °C for 24 h, with stirring, in the dark. The resulting suspension was cooled to room temperature, concentrated to 4 mL and diethyl ether (10 mL) was added with stirring. The solid orange product was subsequently washed with ether (2 x 10 mL) and dried in vacuo. **2** was purified by column chromatography, using CH₂Cl₂ as eluent. Yield: 0.125 g (77 %); ¹H NMR (CDCl₃): δ 7.51 (dd, J=7.5 Hz, 24H), 7.29 (t, J=7.5 Hz, 12H), 7.25 (t, J=7.5 Hz, 24H), 6.48 (d, J=7.5 Hz, 4H, H_a- PhPt((PPh₃)₂I), 6.15 (d, J=7.5 Hz, 4H, H_b-PhPt((PPh₃)₂I), 2.73 (s, 6H), 2.61 (s, 3H), 2.45 (q, J=7.5 Hz 4H), 2.34 (s, 6H), 1.06 (t, J=7.5 Hz, 6H); ¹³C NMR (CDCl₃) δ 152.2, 139.9, 135.9, 135.4, 134.2, 132.6, 131.8, 131.6, 131.3, 130.9, 130.5, 130.3, 128.1, 95.8, 17.9, 17.7, 15.5, 14.5, 13.9; ³¹PNMR (CDCl₃) δ 21.55 (J_{Pt-P}=3078 Hz)

Synthesis of 3 A 10 mL round-bottom Schlenk flask was loaded with 2.0 mg (0.92 μ mol) of 2 which were dissolved in 1.0 mL of CH₂Cl₂ and 33.4 μ L (1.84 μ mol) of AgOTf (55.1 mM in CH₃CN) were added dropwise. The mixture was stirred in the dark. Following a 20 min period, precipitation of white solid was observed and the suspension was filtrated. 3 mL of n-Hexane were added to the filtrate and orange crystalline solid was obtained by slow diffusion of Et₂O. Yield: 2.0 mg (94 %); ¹H NMR (CDCl₃): δ 7.43 (dd, J=6.8 Hz, 12H), 7.39 (t, J=6.8 Hz, 24H), 7.31 (dd, J=6.8 Hz, 24H), 6.35 (s, 6H), 2.62 (s,3H), 2.45 (q, J=7.4 Hz, 4H), 2.35 (s, 6H), 1.07 (t, =7.4 Hz, 6H) ¹³C NMR (CDCl₃) δ 151.7, 136.2, 134.3, 134.2, 134.1, 134.0, 131.7, 131.5, 129.1, 129.0, 128.9, 127.7, 127.3, 118.5, 95.3, 17.3, 15.3, 14.8, 14.6, 13.7 ³¹PNMR (CDCl₃) δ 20.53 (J_{Pt-P}=3007 Hz)

Synthesis of 4 A 10 mL round-bottom Schlenk flask was loaded with 10.0 mg (4.51 μ mol) of **3** which were dissolved in 1.0 mL of CH₂Cl₂ and 132.4 μ L (4.510 μ mol) 4,4'-dipyridine were added (34.10 mM in CH₃CN). The solution was stirred in the dark for 10 min. Orange solid was obtained by slow diffusion of Et₂O in the solution. Yield: 9 mg (84 %) ¹H NMR (CDCl₃) δ 8.18 (b, 24H), 7.27 (b, 360H), 7.04 (b, 24H), 6.48 (d, J=7.5 Hz, 24H), 6.37 (d, J=7.5 Hz, 24H), 2.71 (s, 36H), 2.60 (s, 18H), 2.45 (dd, J=7.0 Hz, 24H), 2.34 (s, 36H), 1.07 (t, J=7.0 Hz, 36H) ¹³C NMR (CDCl₃) δ 152.7, 151.7, 144.2, 139.6, 137.0, 134.1, 132.2, 130.9, 130.7, 130.1, 128.8, 127.4, 127.0, 126.6, 126.5, 124.1, 119.8, 95.2, 94.3, 17.5, 17.3, 15.2, 14.7, 13.7 ³¹PNMR (CDCl₃) δ 20.53 (J_{P-Pt}=3027 Hz)

Full ¹H NMR of 4



Figure S1. The highly symmetric ¹H NMR spectrum of the assembly **4** ($1.0x10^{-4}$ M). *Inset*: full assignment of the repeating molecular fragment (Bodipy - 4,4' -dipyridine)

³¹P{1H} NMR spectra of 2, 3, 4



Figure S2. ³¹P $\{1H\}$ NMR spectra (202.46 MHz, 298 K, CDCl₃) of 2 (red line), 3 (black line) and 4 (blue line).

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2D-ROESY spectrum of 4



Figure S3. 2D-ROESY NMR of **4** (1.0 mM; CDCl₃), showing *intermolecular* cross peaks between the α proton of 4,4'-dipyridine and the phosphine protons of **3**. a) Zoom in the area of interaction of H_{α}-H_{PPh3}

Mass Spectrometry for 4

Experimental section

Electrospray ionization mass spectrometry (ESI-MS) was performed in the positive ionization mode on a LTQ Orbitrap Velos (Thermo Fisher, San Jose, USA) equipped with a heated ESI probe. Samples were dissolved in acetone and 100 μ g/ml solutions were infused at a flow rate of 5 μ l/min. The resolution of the Orbitrap mass analyzer was set to 60000 and 100 scans were averaged.

• The applied high-resolution exact-mass Orbitrap mass analyzer allowed for identification of structure **4** with security due to highly accurate detection of molecular masses and unequivocal assignment of charge states of ion species. This feature of the method was of utmost importance for attributing $[M - 4OTf]^{4+}$ and $[M - 8OTf]^{8+}$ mass signals (Figures S6 and S7, respectively) as their isotopic patterns were superimposed by ESI-generated fragments corresponding to the half of structure **6** detected at identical m/z-values at charge states 2+ and 4+, respectively.



Figure S4. High-resolution electrospray ionization mass spectrum of the hexagonal assembly $4 [M-5OTf]^{5+}$ in acetone.



[M-7OT f]⁷⁺ C₇₀₁H₆₀₆B₆F₁₅N₂₄O₁₅P₂₄Pt₁₂S₅

Figure S5. Experimental (red) and theoretical (solid blue) ESI mass spectra structure 4. The sevenfold charged molecular ion of 4 (dashed red) is superimposed by the isotopic distribution of a quadruply charged fragmentation product of the structure. The fragment is generated during the ESI process. The elemental composition of the fragment is $C_{397}H_{341}B_3F_9N_{13}O_9P_{14}Pt_7S_3$ and its theoretical mass spectrum is displayed in the bottom (dashed blue).





Figure S6 Experimental (red) and theoretical (solid blue) ESI mass spectra structure **6**. The superposition of signals is arising from the quadruply charged structure **4** (dashed red) and a doubly charged fragment of the structure. The fragment is generated during the ESI process and consists of three metal-containing units and three bipyridines, which corresponds to the half of structure **4** ($C_{352}H_{303}B_3F_{12}N_{12}O_{12}P_{12}Pt_6S_4$, theoretical mass spectrum dashed blue line). Both species exhibit the same m/z ratio, but are clearly resolved and assigned by high resolution MS (red).

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Figure S7. Experimental (red) and theoretical (solid blue) ESI mass spectra of structure **4**. The superposition of signals is arising from the eightfold charged structure **4** (dashed red) and a quadruply charged fragment of the structure. The fragment is generated during the ESI process and consists of three metal-containing units and three bipyridines, which corresponds to the half of structure **4** ($C_{350}H_{303}B_3F_6N_{12}O_6P_{12}Pt_6S_2$, theoretical isotopic distribution dashed blue line). Both species exhibit the same m/z ratio, but are clearly resolved and assigned by high resolution MS (red).

Time-resolved Fluorescence Anisotropies

The time-resolved fluorescence depolarization method estimates the rotational correlation time θ which in turn is directly proportional to the volume (Vmol) or molecular weight of the entity via the Stokes-Einstein-Debye (SED) equation.



Figure S8A. Estimation of rotational correlation times of **2** and **4** in CHCl₃ at 23 ⁰C using impulse reconvolution analysis (IRA): The fitting equation is the D(t) = r(t)S(t) in which D(t) and S(t) are respectively the so-called difference (GI_{VV}(t)-I_{VH}(t)) and sum (GI_{VV}(t)+2I_{VH}(t)) functions: I_{VV} is the fluorescence intensity when the excitation and emission polarizers are parallel, I_{VH} is the fluorescence intensity for mutually perpendicular polarizers, and G = I_{HH}(t)/I_{HV}(t) is a correction factor dependent on the emission wavelength. The time-dependent fluorescence anisotropy is given by $r(t) = r_{\infty} + B_1 e^{(-t/\theta)}$; θ stands for the rotational correlation time and r_{∞} is the magnitude of r(t) at long time after pulse excitation. (*Excitation was set to 510 nm. The emission was collected at 540 nm*)

The corresponding goodness of fit i.e., chi-square (χ^2), Durbin-Watson (DW), weighted residuals (WRES) and autocorrelation (AU) are given separately for each curve.



Figure S8B. Estimation of rotational correlation times of **1** and **3** in CHCl₃ at 23 0 C using IRA analysis (see above). Estimated values are $\theta_1 = 0.23 \pm 0.01$ ns and $\theta_3 = 0.25 \pm 0.01$ ns respectively.



Steady-state Fluorescence and Fluorescence-Excitation Anisotropies

Figure S8C. Low temperature (93 K) excitation – fluorescence spectra and excitation - fluorescence anisotropies of **1**, **2**, **3** and **4** in 2MeTHF

Fluorescence Lifetime Measurements



Figure S9A. Fluorescence decay traces and fitting curves of the building block **2** and the hexagonal assembly **4** in CHCl₃ at 23 0 C. Grey circles represent the pulse profile (*excitation at 500 nm; emission was detected at 540 nm*)



Figure S9B. Fluorescence decay traces and fitting curves of the Bodipy **1** and 3 in CHCl₃ at 23 ^oC. (*Excitation at 500 nm; emission was detected at 540 nm*)

X-ray Crystal Structure Determination.

Single crystals suitable for X-ray structure analysis were grown by slow evaporation of a solution of 4 in toluene. The crystal structure of 4 (Fig. 1) was solved by single - crystal X- ray diffraction in the monoclinic space group P21/n. A crystal of 4.2.6(C6H5CH3) $\cdot 0.5$ (H2O) with approximate dimensions $0.06 \times 0.16 \times 0.24$ mm was taken from the mother liquor and immediately cooled to -113 °C. Diffraction measurements were made on a Rigaku R-AXIS SPIDER Image Plate diffractometer using graphite monochromated Cu K α radiation. Data collection (ω -scans) and processing (cell refinement, data reduction, Empirical and Numerical absorption correction) were performed using the CrystalClear program package³. The structure was solved by direct methods using SHELXS-97 4 and refined by full-matrix least-squares techniques on F² with SHELXL-97.⁵ Important crystallographic data are listed in Table S1. Further experimental crystallographic details for 4: $2\theta_{max} = 130^{\circ}$; reflections collected/unique/used, 67068/19045 [Rint = 0.0616]/19045; 1033 parameters refined; $(\Delta/\sigma)_{max} = 0.003$; $(\Delta\rho)_{max}/(\Delta\rho)_{min} = 2.452/-1.379 \text{ e/Å}^3$; R1/wR2 (for all data), 0.677/0.1601. All hydrogen atoms were introduced at calculated positions as riding on bonded atoms. All non-hydrogen atoms were refined anisotropically.

Formula	$C_{124.2}H_{114.8}BI_2N_2O_{0.5}P_4Pt_2$
Fw	2422.05
Space group	$P2_{1}/n$
<i>a</i> (Å)	19.6006(4)
b (Å)	16.7246(3)
<i>c</i> (Å)	35.9977(7)
α (⁰)	90
β (⁰)	96.735(1)
γ (⁰)	90
$V(\text{\AA}^3)$	11719.1(4)
Ζ	4
<i>T</i> (°C)	-113
Radiation	1.54178
$\rho_{calcd}, g \text{ cm}^{-3}$	1.373
μ , mm ⁻¹	9.403
Reflections with $I \ge 2\sigma(I)$	15566
R_{I}^{a}	0.0565
$wR_2^{\ a}$	0.1508

Table S1. Crystallographic data for 4.2.6(C₆H₅CH₃).0.5(H₂O).

^a w=1/[$\sigma^2(F_o^2)$ +(αP)²+bP] and $P = (\max F_o^2, 0)$ +2 F_c)/3, $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$ and $wR_2 = \{\Sigma[w(Fo - Fc)]/\Sigma[w(F_o)]\}$.

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