

Coordination-Driven Self Assembly of a Brilliantly Fluorescent Rhomboid Cavitand Composed of Bodipy-Dye Subunits

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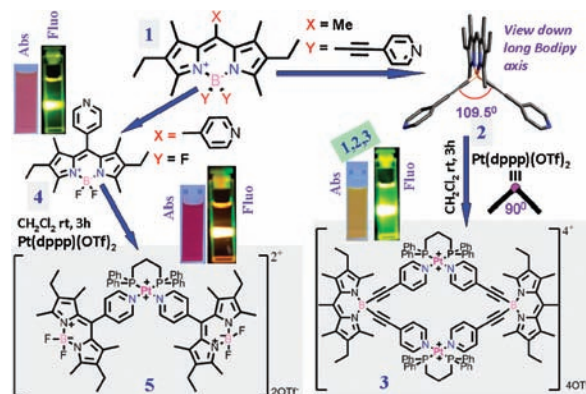
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Abstract: The two sp³ hybridized fluorine atoms of a Bodipy dye have been synthetically replaced with the linear donor ligand 4-ethynylpyridine (–C≡C–Py) to form a rigid and highly symmetrical 109.5° building block in which the fluorophore subunit is vertically aligned to the plane formed by the –C≡C–Py donors. Upon reaction of the above tecton with a 90° organoplatinum acceptor unit, an intensely fluorescent rhomboid cavitand was manifested in solution. In contrast to the vast majority of coordination-driven self-assembled chromophoric systems, the present one fully conserves the excellent photophysical properties of the parent Bodipy dye. These unique features of the present metallosupramolecular entity constitute a fascinating metal-to-ligand self-assembled prototype for building compact and intensely luminescent materials with host–guest capabilities.

Artificial self-assembly has emerged as a potentially powerful platform for performing specific light functions and even mimicking complicated natural photoprocesses.¹ This can be understood by the fact that self-assembly of light (re)active constituents into large superstructures causes the emergence and evolution of new excitonic interactions that cannot be predicted by considering the subcomponents in isolation. One of the major challenges in this context is the design of new compact and intensely luminescent superstructures capable of harvesting light and, subsequently, efficiently managing the concentrated – free of traps – excitonic energy in a controlled and preprogrammed manner for lighting applications (such as accumulation and tuning in fluorescence,² up-conversion of light,³ electronic energy transfer (EET) to a reactive center,^{1,4} EET based sensing systems, etc.¹).

Among the various self-assembly protocols coordination-driven self-assembly has emerged as a powerful new tool to construct stiff and compact metallosupramolecular architectures with a well-defined shape and size.⁵ However, those who seek to harness metal-to-ligand self-assembly to fabricate intensely luminescent superstructured materials find that coordination chemistry brings about dramatic quenching of the local emissive state associated with complex excited state deactivation.⁶ When the metal atom is coordinated directly to the electronically conjugated backbone of a fluorophore, the excitation is either (i) quickly delocalized up to the metal atom leading to weakly emitting charge transfer states or (ii) transferred via an ultrafast intersystem crossing (ISC) to the triplet state (owing to the strong spin–orbit coupling with the metal atom) which then decays nonradiatively to the ground state.⁷ Can the connection topology be cleverly engineered to overcome this

Scheme 1. Schematic Illustration of Supramolecular Synthesis via Coordination-Driven Self-Assembly of Properly Designed Bodipys Donors and the Platinum Triflate 90° Acceptor in Specific Stoichiometric Ratios



problem? Here, we were able to regulate synthetically the connectivity of the popular class of the boron dipyrromethene dyes (Bodipys) with a versatile pyridine donor, to form a unique tecton capable of creating highly emissive 3D metallosupramolecular assemblies upon reaction with a proper organometallic acceptor.

The design rationale for a strongly luminescent assembled cavitand is illustrated in Scheme 1. The luminescent subunit **1** (i.e., the Bodipy dye itself) is known to have several exciting and beneficial photophysical features for multipurpose applications.^{3,8} Collectively, Bodipy dyes exhibit bright photoluminescence with quantum yields (Φ) approaching unity, high photo- and chemostability, high extinction coefficients ($\epsilon_{\text{max}} \sim 10^5 \text{ M}^{-1} \text{ cm}^{-1}$), sharp absorption-fluorescence spectra, high fluorescence polarization, extraordinary color tunability by appropriate exocyclic substitution, and/or extension of the π -conjugation. Most importantly for our purpose, the sp³ hybridized fluorine atoms of **1** (i.e., disconnected to the conjugated electronic frame) can be synthetically replaced by appropriate functional rigid donors, e.g. 4-ethynylpyridine (–C≡C–Py), leading to highly symmetric and rigid 3D molecular platforms, e.g. **2**, in which the Bodipy subunit is vertically aligned to the plane formed by the linear –C≡C–Py donors (Scheme 1). Interestingly, when the building blocks 109.5° **2** and 90° platinum triflate Pt(dppp)(OTf)₂ are reacted in a stoichiometric ratio of 2:2 in CHCl₃ or CH₂Cl₂ the formation of a brilliantly fluorescent rhomboidal shaped cavitand (**3**) is manifested, although it is not predicted by strictly considering the angular “combinatorial” capability of the “Molecular Library” for preprogrammed assemblies.^{5c,h}

The verification of the assembled entity in solution was made by ESI-MS, ³¹P, ¹H, ¹³C multinuclear NMR analysis and fluorescence spectroscopy methods. Single crystals suitable for X-ray structure analysis were grown by diffusing diethyl ether into **3** in

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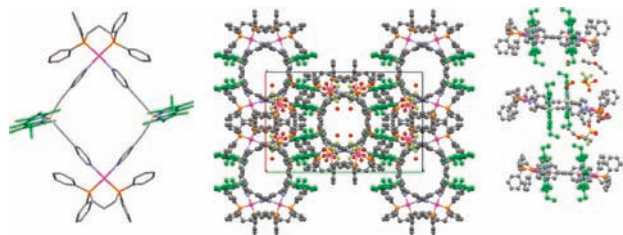


Figure 1. Crystal structure (left) and packing (middle) viewed down *c* crystallographic axis; (right) stacking of **3** into columns (side view). The Bodipy chromophore is colored green for clarity; C, gray; N, blue; Pt, magenta; P, orange; B, pink; O, red; S, yellow; F, light-green. Hydrogens atoms are not shown.

CH_2Cl_2 . The crystal structure of **3** was solved by single-crystal X-ray diffraction in the monoclinic space group $C2/c$ (Figure 1). The rhomboidal shaped planar frame exhibits diagonals of 14.1 and 11.5 Å formed respectively between Pt–Pt and boron–boron centers. The crossing point of the diagonals is the inversion center of the centrosymmetric structure. The long axes of the two bodipy subunits are mutually perpendicular to the rhomboid plane and accordingly parallel to each other. An appreciable distortion of the N–Pt–N angle (85.1°) relative to the ideal 90° was observed whereas the sp^3 hybridized boron corners remain nearly invariable (110.3°). The assembled members in **3** are held together through considerable tension which is concentrated and distributed across nearly all angular parts in one of the two boron–ethynylpyridine–platinum (B–C≡C–Py–Pt) arms (per tecton **2**), i.e., $\angle(\text{B–C}\equiv\text{C}) = 174.9^\circ$; $\angle(\text{–C}\equiv\text{C–Py}) = 173.9^\circ$; $\angle(\text{centroid pyridine–N–Pt}) = 176.9^\circ$. The rhomboid cavitands are stacked along the *c*-axis forming nanosized channel-like cavities with an inter-ring Pt–Pt distance of ~ 14.7 Å. Adjacent rings in a column are offset by $\sim 21^\circ$ with respect to one another. This leads to sheets in which the neighbor Bodipy subunits of the alternate rhomboids face parallel (~ 3.7 Å) to each other sliding slightly along the short Bodipy axis (Scheme S1; Supporting Information (SI)). The triflate anions are positioned outside the cavity space.

Neither replacement of the fluorine atoms of **1** with the 4-ethynyl pyridine fragment (donor **2**) nor subsequent coordination of **2** with platinum triflate to form **3** perturbs the emitting electronic state of the parent Bodipy dye **1** in solution (see Scheme 1 and Table S1 of the SI). This allows the assembled system to conserve the exceptional photophysical features of the precursory compounds (**1**, **2**) namely, $\epsilon_{\text{max}} \sim 78\,000\ \text{M}^{-1}\ \text{cm}^{-1}$ (per dye unit), high quantum yield ($\Phi = 0.86$), fluorescence lifetime $\tau = 6.9$ ns, and high fluorescence anisotropy $r \approx 0.37$ (vide infra). On the contrary, when the compound **4** (in which a pyridine group is directly attached to the conjugated Bodipy's backbone) reacts with Pt(dppp)(OTf)₂ in a stoichiometry of 2:1 in CH_2Cl_2 to form **5**, the findings suggest the presence of significant intramolecular charge transfer effects such as considerable broadening and red shifting of the absorption and fluorescence spectra with a concomitant dramatic decrease of Φ from 0.47 (**4**) to ~ 0.06 (**5**) (see Table S1 and Figure S5 of the SI).

The rigidity and stiffness of **3** are maintained in fluid and glassy media as confirmed by fluorescence polarization spectroscopy. The fact that the absorption–emission (S_0 – S_1) electronic transition dipoles of the Bodipy chromophore are polarized along the long molecular axis¹⁰ allows for detailed structural verification of the metallosupramolecular cavitand **3** in solution. In a frozen 2-methyl THF solution of **3** (0.70 μM) at 93 K, when molecular tumbling has ceased, the steady-state fluorescence anisotropy r_{ss} of the above assembled chromophoric system reaches the value 0.37, that is, the limited value of the isolated

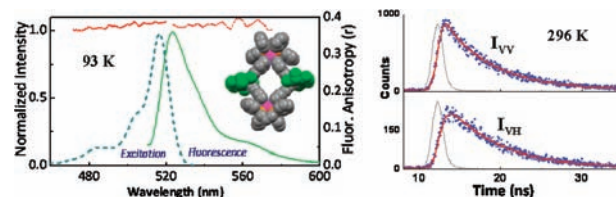


Figure 2. Left: Low temperature (93 K) excitation – fluorescence spectra and excitation – fluorescence anisotropies (red lines) of **3** in 2MeTHF. Right: Spherical rotor anisotropy model: Simultaneous fit of both the parallel (I_{VV}) and crossed (I_{VH}) decay components of **3** in Cl_2HCCl_2 at 296 K; exc. 518 nm. Red lines: best fitting curves ($\chi^2 = 1.12$); Gray lines: instrument response function.

Bodipy unit (see Table S1 of the SI). The fact that we see no loss of fluorescence polarization for **3** – although Förster's EET between the two assembled Bodipys is strongly expected (homotransfer)^{11,12} – definitely demonstrates no distortion of the parallel chromophoric alignment¹³ of **3**. No aggregation phenomena were observed in a good solvent such as tetrachloroethane at ambient temperatures, as demonstrated by time-resolved fluorescence depolarization spectroscopy in conjunction with the Stokes–Einstein–Debye (SED) equation. By applying the spherical rotor anisotropy model¹⁴ to the experimental I_{VV} and I_{VH} data of **3** at 23 °C, the rotational reorientation time τ_r of **3** (0.70 μM) was determined to be 655 ± 40 ps (Figure 2 and SI). This experimental value corresponds to a rotating spheroid with a molecular volume of ~ 1690 Å³ which is in accordance, within experimental error, with the one calculated from the monomeric unit of the X-ray crystal structure of **3** (~ 1780 Å³ including van der Waals radii).

In summary, we herein report the formation and manifold characterization of a unique, brightly fluorescent metallosupramolecular rhomboid cavitand composed of a properly designed 109.5° Bodipy-dye donor and a 90° platinum acceptor. The connection topology of the fluorescent building block has been suitably engineered to completely eliminate exciton traps. These tectons may appear challenging for building compact photonic materials, as their $\sim 109^\circ$ angular capability can lead, via well-established metal-to-ligand assembly protocols,⁵ to the facile construction of a rich variety of 3D nanocages with intensely luminescent outer shells such as cuboctahedra, adamantanoids, trigonal bipyramides, etc.

Supporting Information Available: Synthetic procedures; NMR, ESI-MS data, spectroscopic, and crystallographic data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (13) Bodipy dyes exhibit a large Förster distance for energy homotransfer of about 57 Å. For the present assembly in which the two chromophoric centers of mass are separated by ~ 14 Å, electronic energy exchange should be very fast (ca. $k_{\text{EET}} \approx (1-4) \times 10^{12} \text{ s}^{-1}$ depending on the mutual orientation) compared to the deactivation rate of the excited state $k = 1.7 \times 10^8 \text{ s}^{-1}$. Since the fluorescence anisotropy is not affected by the EET we conclude that the Bodipy dipoles in **3** do not deflect at all from their mutual parallelism.
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