

Communication

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*J. Am. Chem. Soc.*, **Just Accepted Manuscript** • Publication Date (Web): 03 Sep 2019

Downloaded from pubs.acs.org on September 3, 2019

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# Self-Assembled Fluorescent Pt(II) Metallacycles as Artificial Light-Harvesting Systems

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*Supporting Information Placeholder*

**ABSTRACT:** Light-harvesting is one of the key steps in photosynthesis, while, developing artificial light-harvesting systems (LHSs) with high energy transfer efficiencies has been a challenging task. Here we report fluorescent hexagonal Pt(II) metallacycles as a new platform to fabricate artificial LHSs. The metallacycles (**4** and **5**) are easily accessible by coordination driven self-assembly of a triphenylamine-based ditopic ligand **1** with *di*-platinum acceptors **2** and **3**, respectively. They possess good fluorescence properties both in solution and in the solid state. Notably, the metallacycles show aggregation induced emission enhancement characteristics (AIEE) in a DMSO-H<sub>2</sub>O solvent system. In the presence of a fluorescent dye Eosin Y (ESY), the emission intensities of the metallacycles decrease but the emission intensity of ESY increases. The absorption spectrum of ESY and the emission spectra of the metallacycles show a considerable overlap, suggesting the possibility of energy transfer from the metallacycles to ESY, with an energy transfer efficiency as high as 65% in the **4**+ESY system.

Photosynthesis is the main energy source for the survival of the living world. The natural photosynthesis process that takes place in the green plants and other organisms starts with the absorption of light energy (sunlight) by a large number of closely packed green pigments chlorophyll, embedded in a complex known as antenna protein or light-harvesting complex.<sup>1</sup> Subsequently, the absorbed energy funnels through chlorophylls to the reaction center where light energy transforms into chemical energy (carbohydrates, like sugar). Inspired by nature chemists have developed several artificial light-harvesting systems (LHSs) to understand the key aspects of the process, intricacies of the mechanism along with their potential applications in photosynthesis, photocatalysis, and photovoltaics. In this context, wide varieties of scaffolds such as dendrimers,<sup>2</sup> organo or hydrogels,<sup>3</sup> vesicles,<sup>4</sup> micelles,<sup>5</sup> host-guest assemblies,<sup>6</sup> metal-organic frameworks,<sup>7</sup> organic polymers<sup>8</sup> and so on have been utilized in the last few years.

There are two prime factors that one should take into account to achieve high energy collection efficiency in LHSs: I) the system should possess multiple donors per acceptor and II) the donors

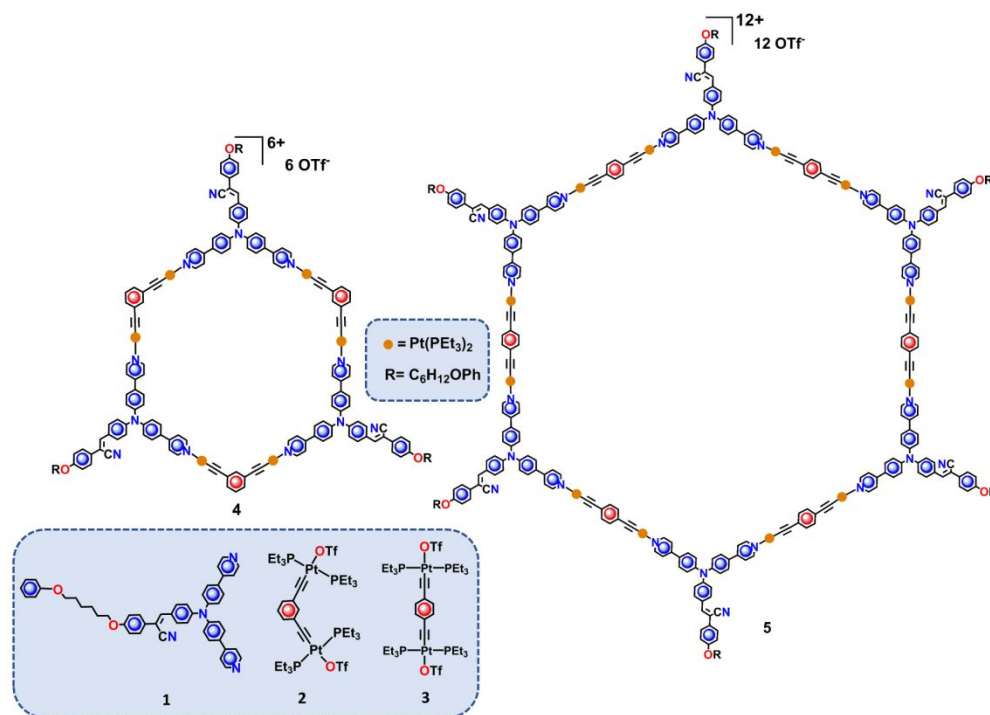
should not suffer fluorescence quenching in their closely packed arrangements.

The LHSs reported to date could be broadly classified into two categories: a) covalently bonded networks and b) self-assembled architectures. The former one has the advantage of providing a stable platform but it needs laborious synthetic steps. In contrast, self-assembled architectures could be easily obtained by mixing appropriate building blocks under suitable conditions. Therefore, supramolecular coordination complexes (SCCs) with easy synthetic accessibility, well-defined shapes, sizes, easy solution processability and tunable photophysical properties could be interesting materials for light harvesting.

Over the past few decades several SCCs like one dimensional (1D) helices, two dimensional (2D) polygons and three-dimensional (3D) polyhedrons have been developed utilizing the directional coordination bonding approach.<sup>9</sup> Such SCCs are found to be attractive materials owing to their widespread applications in catalysis,<sup>10</sup> sensing,<sup>11</sup> biomedical science,<sup>12</sup> proton conduction,<sup>13</sup> and so on. Although several luminescent platinum based metallacycles and cages have been reported,<sup>14</sup> their application towards light harvesting is in its infancy.<sup>15</sup> We report here two new fluorescent hexagonal platinum (II) metallacycles **4** and **5** (Figure 1), along with their light-harvesting properties.

The desired metallacycles were designed and synthesized from ditopic organic donor **1** and *di*-platinum (II) acceptors **2** and **3** (Figure 1). Ligand **1** has a triphenylamine core with a cyanostilbene moiety decorated with an alkyl chain bearing a phenyl group, which could facilitate supramolecular assembly formation through non-covalent interactions.<sup>16</sup> The cyanostilbene moiety has interesting optical properties of aggregation induced emission enhancement (AIEE), as a result of their restricted rotation in the aggregate state.<sup>17</sup> Moreover, the cyanostilbene moieties promote self-assembly to form various nano-architectures. Accordingly, the metallacycles may easily form supramolecular assemblies, and in their closely packed state will not suffer fluorescence quenching and thus, could serve as an excellent platform for light harvesting.

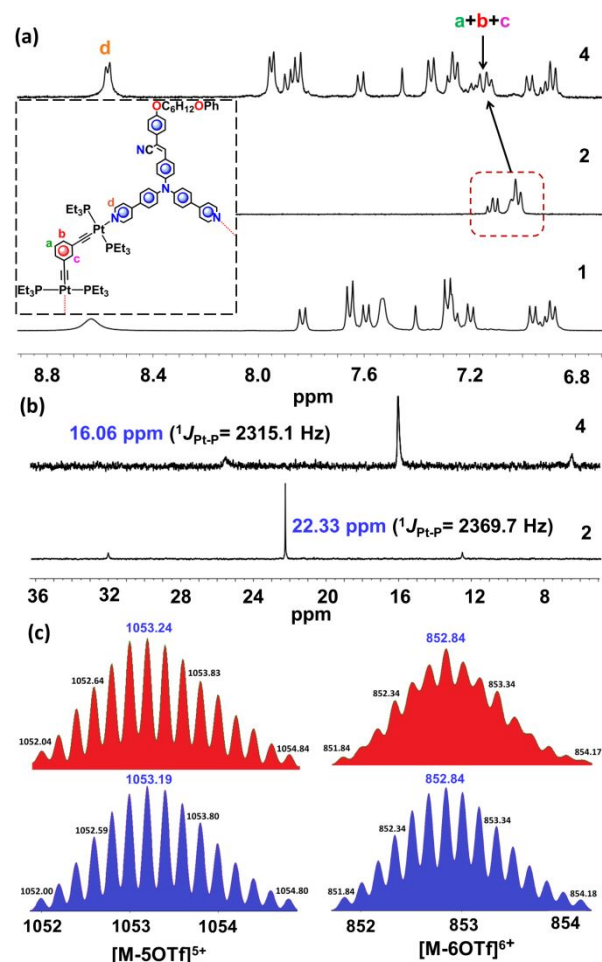
The hexagonal [3+3] metallacycle **4** was readily accessible by stirring an equal molar mixture of **1** and Pt-acceptor **2** in a mixed solvent system of dichloromethane-methanol (1:1; v/v) at



**Figure 1.** Metallacycles **4**, **5** and the building blocks **1**, **2**, and **3**.

room temperature for 6 h; a [6+6] metallacycle **5** was obtained from **1** and Pt-acceptor **3**, under similar reaction conditions (Schemes S2 and S3). The metallacycles were obtained as yellow solids upon addition of diethyl ether onto the reaction mixtures, and were characterized by various spectroscopic techniques like  $^1\text{H}$  NMR,  $^{31}\text{P}\{^1\text{H}\}$  NMR,  $^1\text{H}$ - $^1\text{H}$  COSY, 2D diffusion-ordered  $^1\text{H}$  NMR spectroscopy (DOSY), and electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS) analysis (Figures S1-S14).

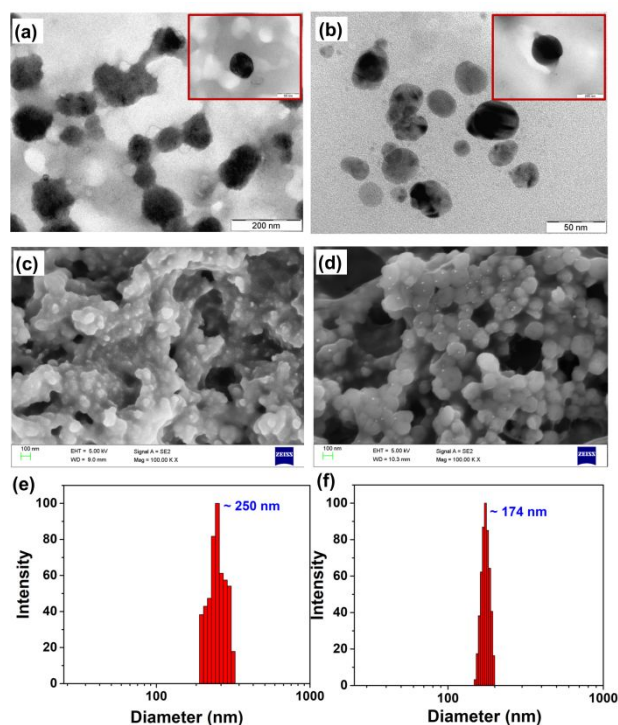
In the  $^1\text{H}$  NMR spectrum of **4** characteristic NMR signals corresponding to **1** and the Pt acceptor **2** observed at around 8.57 ppm and 7.12-7.19 ppm respectively with a 1:1 intensity ratio indicated the formation of [3+3] assembly (Figures 2a and S4). Similarly, metallacycle **5** formation was indicated by  $^1\text{H}$  NMR signals with a 1:1 intensity ratio corresponding to the ligand **1** and Pt-acceptor **3** at around 8.56 ppm and 7.19 ppm respectively (Figure S8). The  $^{31}\text{P}\{^1\text{H}\}$  NMR of both metallacycles displayed sharp singlet peaks (Figures 2b and S9) with concomitant  $^{195}\text{Pt}$  satellites ( $\delta$  = 16.06 ppm and 16.30 ppm for **4** and **5** respectively), which indicated the presence of only one type of phosphorus in the assemblies, confirming the formation of highly symmetric structures. An upfield shift of  $\sim 6$  ppm was observed in the  $^{31}\text{P}\{^1\text{H}\}$  NMR of the metallacycles with respect to their corresponding Pt-building blocks, attributed to the metal-ligand coordination. The stoichiometry of the formation of metallacycles **4** and **5** was confirmed by ESI-TOF-MS analysis. For metallacycle **4**, isotopic patterns of the peaks at  $m/z$  1053.24 Da and 852.84 Da for the  $[\text{M}-5\text{OTf}]^{5+}$  and  $[\text{M}-6\text{OTf}]^{6+}$  respectively matches well with their calculated isotopic distribution patterns (Figure 2c). In contrast, the larger metallacycle **5** shows a peak at  $m/z$  1186.82 Da for  $[\text{M}-9\text{OTf}]^{9+}$ , however, the isotopic distribution pattern suggests that the peak is actually due to two fragments  $\text{X}^{3+}$  and  $\text{Y}^{6+}$  (Figures S11 and S12) resulting from  $[\text{M}-9\text{OTf}]^{9+}$ .



**Figure 2.** (a)  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) and (b)  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.4 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) spectra of the metallacycle **4** and its building blocks, (c) experimental (red) and calculated (blue) ESI-TOF-MS spectra of **4**.

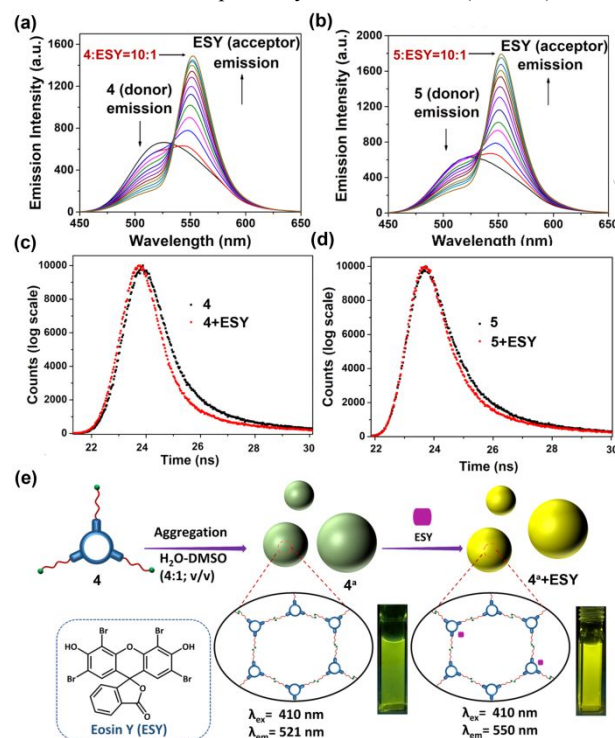
Moreover, single diffusion bands at  $7.6 \times 10^{-9}$  m<sup>2</sup>/sec and  $3.6 \times 10^{-9}$  m<sup>2</sup>/sec in the <sup>1</sup>H DOSY NMR spectra (Figures S13 and S14) of **4** and **5** respectively are in agreement with the formation of a single product in the reaction. To gain further insight into the structural characteristics of the metallacycles PM6 semi-empirical calculations were carried out, where the ethyl groups of the phosphine ligands were modeled as hydrogen atoms. The computational results indicate that the metallacycles have an almost planar hexagonal backbone, with internal cavity sizes of around 3.2 nm and 6.6 nm for **4** and **5** respectively (Figures S15 and S16).

The photophysical properties of the metallacycles were investigated in DMSO. The UV-Vis spectrum of **4** exhibits two absorption bands at around 300 nm and 400 nm, whereas, **5** has absorption bands at around 340 nm and 400 nm (Figure S17 and S18). Upon excitation at 410 nm both metallacycles display similar emission pattern with an emission maximum at 521 nm (Figure S19). The absorption and emission of the metallacycles were also investigated in various solvents, which did not indicate any significant solvatochromic characteristics (Figure S20). With increasing water content in the DMSO solution of the metallacycle (**4** or **5**), a substantial increase in fluorescence intensity is observed (Figures S21 and S22), as expected due to the presence of the cyanostilbene moieties that facilitate AIEE. The highest emission intensity was observed in 80% H<sub>2</sub>O/DMSO, while further increase in water fraction leads to a decrease in emission intensity, presumably due to the precipitation of the metallacycles. This AIEE behavior is also supported by a sharp increase in fluorescence quantum yields ( $\phi$ ) of the metallacycles in the solid-state and in the aggregates (**4**<sup>a</sup> and **5**<sup>a</sup>). For instance, fluorescence quantum yield of **4** was found to be 28 % in the solid-state and 17 % in a H<sub>2</sub>O-DMSO (4:1; v/v) solvent system, which are substantially higher than the quantum yield of the metallacycle in the DMSO solution ( $\phi$  = 9 %). A similar trend was observed in metallacycle **5**, which has fluorescence quantum yields of 33 %, 28 % and 10 % in the solid-state, H<sub>2</sub>O-DMSO solvent system (4:1; v/v) and in a DMSO solution respectively (Table S1).<sup>18</sup>



**Figure 3.** TEM images of (a) **4**, (b) **5**, SEM images of (c) **4**, (d) **5**, and DLS profiles of (e) **4**, (f) **5** in H<sub>2</sub>O-DMSO (4:1; v/v). Insets: TEM image of a single spherical particle.

The morphologies of the metallacycles in the aggregated state were investigated by scanning electronic microscopy (SEM) and transmission electron microscopy (TEM). The TEM analysis (Figures 3a and 3b) shows the formation of spherical particles, while the SEM analysis suggests an agglomeration of these spherical particles (Figure 3c and 3d). Dynamic light scattering (DLS) experiments (Figures 3e and 3f) provided average hydrodynamic diameters of the aggregates of around 250 nm and 174 nm for **4** and **5** respectively in H<sub>2</sub>O-DMSO (4:1; v/v).



**Figure 4.** Fluorescence spectra of the metallacycles (a) **4** and (b) **5** with gradual addition of ESY ( $\lambda_{ex}$  = 410 nm) in H<sub>2</sub>O-DMSO (4:1; v/v). Change in the fluorescence decay profiles of the metallacycles (c) **4** and (d) **5** in presence of ESY (metallacycle: ESY = 20:1) in H<sub>2</sub>O-DMSO (4:1; v/v). (e) A cartoon representation of light harvesting system generated from **4** and ESY, with visible color change of the solution under 365 nm UV light in H<sub>2</sub>O-DMSO (4:1; v/v).

These results indicated that a H<sub>2</sub>O-DMSO (4:1; v/v) solvent system would be the best medium to investigate the light-harvesting property of the metallacycles, as under such aggregated state the metallacycles showed the highest fluorescence emission without any self-quenching and precipitation from the solution. To prepare the LHSs we used the fluorescent dye Eosin Y (ESY) as a fluorescence energy acceptor. It is worth noting that for efficient energy transfer the absorption band of the acceptor should overlap with the emission band of the donor. The UV-Vis spectrum of ESY in H<sub>2</sub>O-DMSO has an absorption band from 430 nm to 550 nm with an absorption maximum at 520 nm. As shown in Figure S23 the absorption spectrum of ESY and the emission spectra of the metallacycles overlap well, suggesting the possibility of energy transfer from the metallacycles to ESY. When a 1  $\mu$ M solution (H<sub>2</sub>O-DMSO, 4:1, v/v) of ESY was gradually added to a 3 mL 1  $\mu$ M solution (H<sub>2</sub>O-DMSO, 4:1, v/v) of a metallacycle (**4** or **5**), a sharp decrease in emission intensity of the metallacycle was observed (Figures 4a and 4b), and the fluorescence intensity corresponding to ESY was found to increase upon excitation at 410 nm. In contrast, under



similar condition, ESY alone was found to be non-emissive upon excitation at 410 nm (Figure S24), ruling out the possibility of direct excitation of ESY. Moreover, a substantial increase in the quantum yields of the metallacycles was observed in the presence of ESY, which suggests that ESY accepts and emits most of the excitation energy. The energy transfer efficiencies are calculated as 65 % and 52 % in the 4<sup>+</sup>+ESY and 5<sup>+</sup>+ESY systems respectively at a 10:1 donor/acceptor ratio, which are comparable with some of the recently reported single molecule based supramolecular light-harvesting systems.<sup>15,19</sup>

The best way to understand the energy transfer process is to measure the fluorescence lifetime of the donor in the presence of the acceptor. Therefore, fluorescence decay experiments were carried out to support the occurrence of the light-harvesting process. The fluorescence lifetime of the metallacycle **4** ( $\tau_1 = 0.75$  ns and  $\tau_2 = 2.94$  ns) was found to be higher than the fluorescence lifetime of **4** in the presence of ESY ( $\tau_1 = 0.51$  ns and  $\tau_2 = 2.65$  ns) (Figure 4c). Similarly, the fluorescence lifetime of the assembly of **5** and ESY ( $\tau_1 = 0.57$  ns and  $\tau_2 = 2.86$  ns) was found to be shorter (Figure 4d) than the fluorescence lifetime of **5** ( $\tau_1 = 0.75$  ns and  $\tau_2 = 2.97$  ns). These results indicate that the energy transfer takes place from the metallacycle to the ESY (Figure 4e).

In conclusion, two fluorescent hexagonal metallacycles (**4** and **5**) were devised to construct artificial light-harvesting systems. The metallacycles were found to have good fluorescence properties and AIEE characteristics. Most importantly, simple mixing of the acceptor (Eosin Y) and a metallacycle, results in an efficient Förster resonance energy transfer (FRET) process between the metallacycle and ESY, leading to the in-situ formation of an efficient artificial LHS. These artificial LHSs exhibit good energy transfer efficiencies, as high as 65% in the 4<sup>+</sup>+ESY system at a 10:1 donor/acceptor ratio. We anticipate that understanding the light-harvesting properties in such supramolecular coordination complexes will open up new possibilities for the design and fabrication of LHSs in the future.

## ASSOCIATED CONTENT

### Supporting Information

Experimental details and characterization data of all new compounds.

The Supporting Information is available free of charge on the <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interests.

## ACKNOWLEDGMENT

P.J.S. thanks the U.S. National Institutes of Health (Grant R01 CA215157) for financial support. P.S.M. thanks the SERB (India) for financial support (Grant No. CRG/2018/000315). S.B. thanks CSIR India for research fellowship. K. A. is thankful to Heng Wang and Ruidong Ni for their help in ESI-TOF-MS analysis.

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