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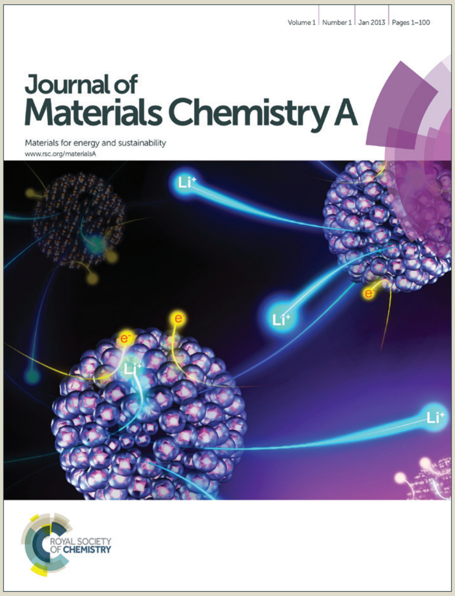

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PAPER

Synthesis of novel platinum complex core as a selective Ag^+ sensor and its H-bonded tetrads self-assembled with triarylamine dendrimers for electron/energy transfers

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A novel platinum complex **PtC** with tri-armed uracil hydrogen-bonded (H-bonded) unit was synthesized via modular synthetic approach and well characterized by ^1H, ^{13}C NMR and MALDI-TOF mass spectroscopies. Two H-bonded tetrads **PtC-(TPAD1)$_3$** and **PtC-(TPAD2)$_3$** based on a metal core **PtC** complexed with two generations of triarylamine dendrimers **TPAD1** and **TPAD2** (with electron-donating nature) were successfully constructed with improved organic solubility via classical H-bonded self-assembly approach. The presence of supramolecular H-bonding in solution and solid state were elucidated by ^1H NMR titrations, IR spectral studies and time resolved photoluminescence (TRPL) measurements. The electron/energy transfers as well as the self-assemblies of supramolecular tetrads were established by UV-Vis and PL titrations and AFM morphological studies. Furthermore, metal complex core **PtC** showed a selective sensitivity towards Ag^+ ions through fluorescence turn-off responses without any interference from other common metal ions. The 1:1 binding stoichiometry and complexation mechanism between probe and Ag^+ ion was established by ^1H NMR titration. Moreover, the PL reversibility of **PtC**+Ag^+ was achievable upon the addition of PMDTA.

Introduction

The design of functional macromolecular structures and supramolecular metal complexes, by the exploitation of self-assembly of complementary components via spontaneous and reversible supramolecular interactions, has long been promised to create myriads of fascinating molecular architectures.[1-3] The supramolecular interactions have many advantages such as (1) nanoscale ordering morphology effectively controlled by supramolecular interactions of active layers to move beyond the trial and error tuning of the device; (2) long-range order introduced to restore high charge-carrier mobilities for the flexibility of the device, which benefited from amorphous materials and potentially cost effective to manufacture; (3) a direct method for assembling large numbers of molecules into structures via supramolecular organization that can bridge length scales from nanometers to macroscopic dimensions for efficient long distance charge transport; (4) controlling precise architectures by the type and number of interactions (e.g. the photosynthetic reaction center in bacteria), where more flexible systems are tolerant of physical deformations, such as cellular lipid bilayers membranes.[4-6]

In the realm of modern supramolecular architectures, metal centered assemblies (**MCs**) governed by non-coavlent interactions are one of the promising candidates in designing functional electronic materials.[7,8] Molecular organizations of these complexes regulated by a wide variety of non-covalent interactions are often ubiquitous in nature and play pivotal roles in many fields like oxygen transport, gene activation, pharmaceuticals and catalysis.[9-10] However, such functional supramolecular entities constituted with hydrogen-bonds and metal complexes are more specific and highly directional in both solutions and surfaces, so they are widely exploited in the construction of three-dimensional supramolecular architectures in both chemical and biological systems.[11] However, both of them have some advantages such as (1) convenient approaches towards precisely controlling the geometries of electron donor-acceptor assemblies via hydrogen-bonded (H-bonded) interactions;[12a,b] (2) 2.5-fold enhancement in photocurrent of photo-electrochemical devices incorporating components possessing complementary H-bonded units;[12c,d] (3) enhancement of electron and hole transport as well as stability and even colors (pure colors to white light)

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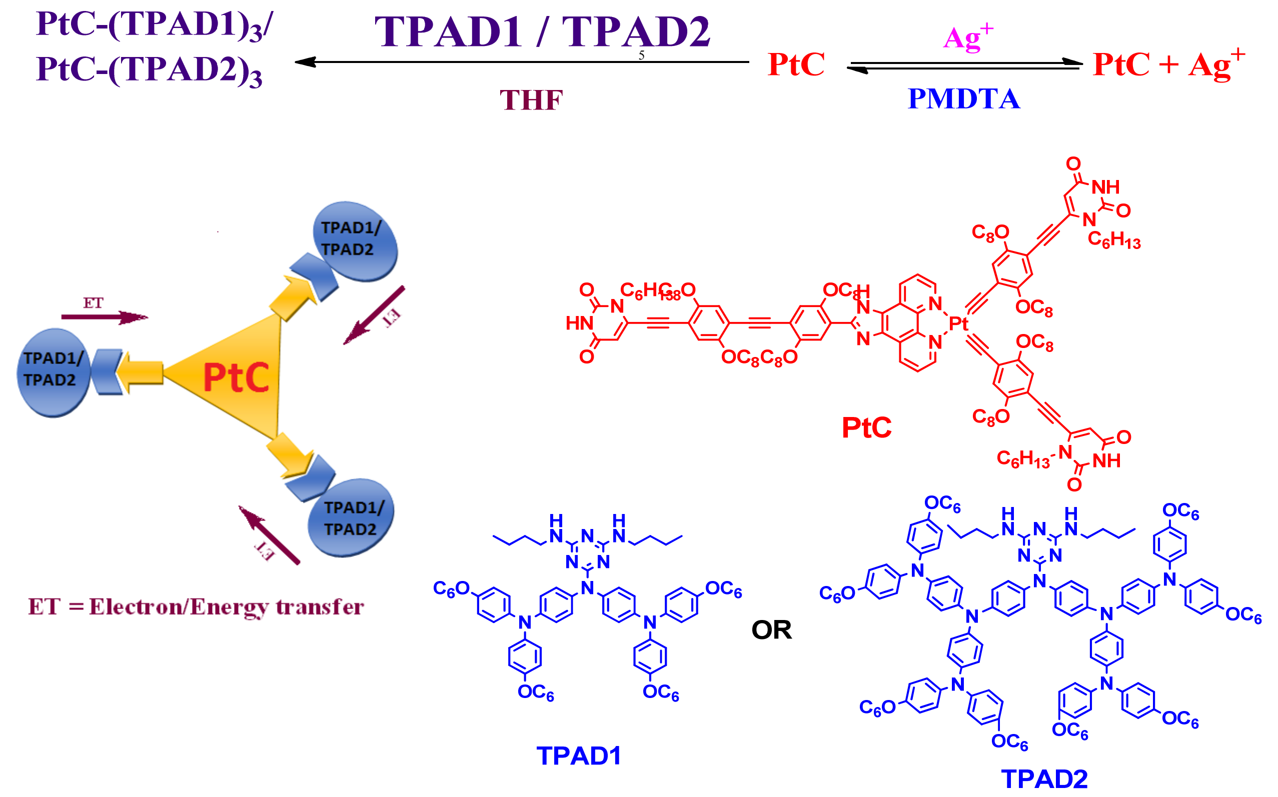


Fig. 1 Schematic representation of **PtC** sensor selectivity towards Ag^+ and chemical structures of supramolecular tetrads **PtC-(TPAD1)$_3$** and **PtC-(TPAD2)$_3$** containing a platinum complex core (**PtC**) and two generations of three triarylamine dendrimers (**TPAD1** and **TPAD2**).

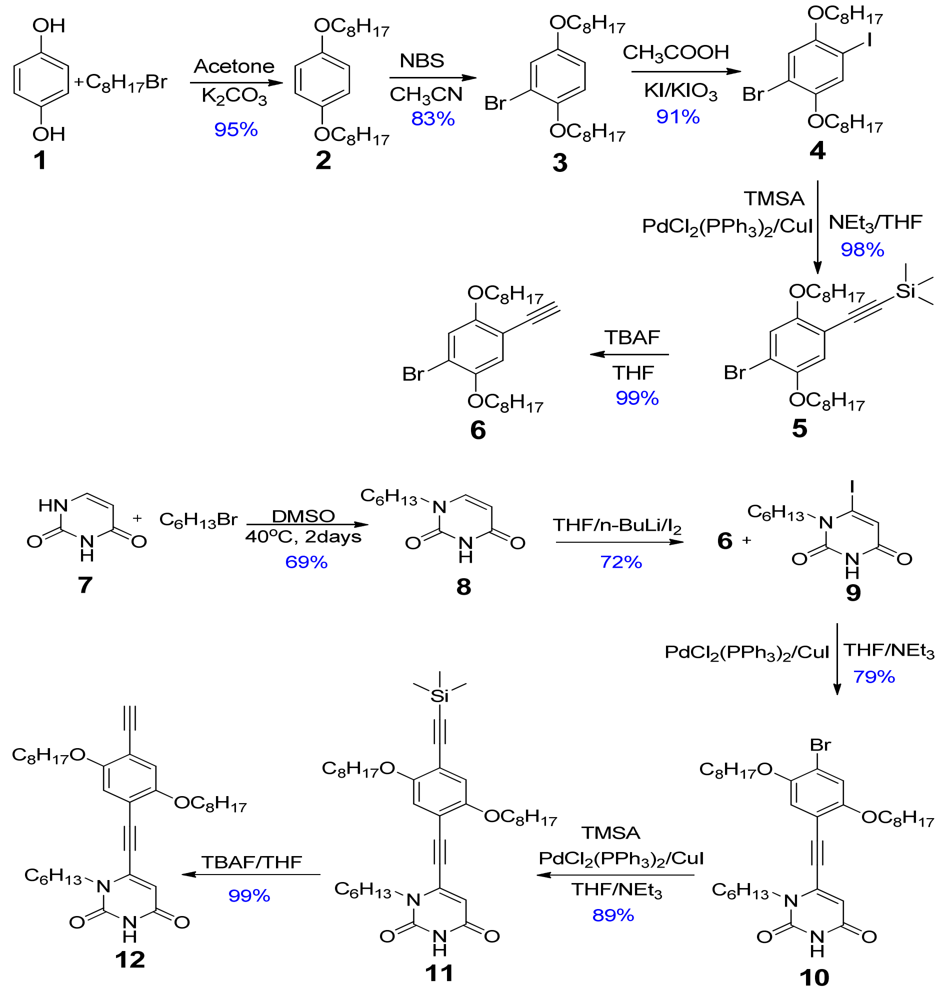
potentially achieved in metal complexes as active layers;[12e,f] (4) high thermal stabilities as well as greater charge transporting properties such as MLCT provided by metal complexes.[12g,h]

Recently, transition metal-based supramolecular **MCs** have been emerged as a specical area in supramolecular chemistry since they play crucial roles in catalysis, molelar-based electronic devices and well defined nanostructures at a molecular level.[2b,13] Among these intriguing metals, platinum has been pierced into daily usage rapidly owing to its anticancer chemotherapy applications.[14] Despite of neurotoxicity caused by platinum drugs, a third-generation platinum drug oxaliplatin was approved for the treatment of metastatic colorectal cancer by US food and drug administration (FDA).[15] Apart from chemotherapy usages platinum-based supramolecular MCs were more reliable sources to build next generation molecular devices. Xing et al reported amphiphilic cationic platinum (II) terpyridyl ferrocene complex to form host-guest driven a self-assembled vesicle structure.[16] Shirakawa et al demonstrated the formation of one-dimensional structure by using π-π and solvophobic interactions of 8-quinolinol platinum (II) chelate derivative with 3,4,5(n-dodecyloxy)benzoylamide unit.[17]

Dendrimers have long been proven as ideal flat-forms in designing multidimensional and multifunctional supramolecular hierarchical nano-architectures due to their high branching points with an easily achievable molecular symmetry at nanoscale.[18] Inherent directional excitation energy transfer (EET) capabilities of dendrimers carved to prepare light-harvesting (LH) antennas in artificial photosynthesis. Dendritic nano-structured self-assemblies are prime constituents in fabricating novel nano-technological electronic devices.[19] Moreover, new bottom-up synthetic approaches for dendritic **MCs** nanostructures with controls over the sizes, surface properties, solubilities and compositions are highly desirable to make intriguing hierarchical **MCs**-based self-assemblies. Shelnutt et al reported the first controlled photo-catalytic approach for synthesizing sheet-like nanodendrites or foam-like nano-sheets of platinum.[20] However, to the best of our knowledge a platinum complex core containing three peripheral uracil H-bonded units in creating **MCs**-based self-assemblies to engineer electron/energy transfer features have not been explored yet.

Metal-based organic complexes are long used in molecule sensing applications because of their flexible energy transfer characteristics.[21] Apart from their conventional applications in various fields transition metals posed a great threat to human health and environmental pollution over recent years. Silver ions often prone to bind with various metabolites, including carboxyl, amine, imidazole and sulfhydryl enzymes.[22] Extreme bioaccumulation and ghastly toxic effects of silver ions make them as intriguing targets to detect selectively.[23] Perversely many small molecule-, polymer- and nanoparticle-based probes have been reported for silver ion detections,[24] but often those probes showed low sensitivities. Thus, it is highly imperative to develop new metal complex-based probes for the selective and sensitive detections of silver ions.

Herein, as shown in Fig. 1, we developed two H-bonded tetrads **PtC-(TPAD1)$_3$** and **PtC-(TPAD2)$_3$** containing a central platinum complex (**PtC**) and two generations of terminal triarylamine dendrimers (**TPAD1** and **TPAD2** with electron-



Scheme 1. Synthetic procedure of compound **12**.

donating nature). We also studied the electron/energy transfers and self-assemblies of H-bonded tetrads by UV/Vis, PL, ^{1}H NMR titrations, TRPL and AFM morphological studies. For the first time we evaluvated the sensing ability of metal complex core (**PtC**) with three uracil units in specific sensing of various metal ions, in which **PtC** core selctively recognized Ag^{+} ions via binding wih imidazole -NH unit, which was verified by NMR-titrations. Importantly, the sensing mechanism of metal complex core was completely reversible upon the addition of a tridentate ligand 1,1,4,7,7-pentamethyl-diethylenetriamine (PMDTA) solution.

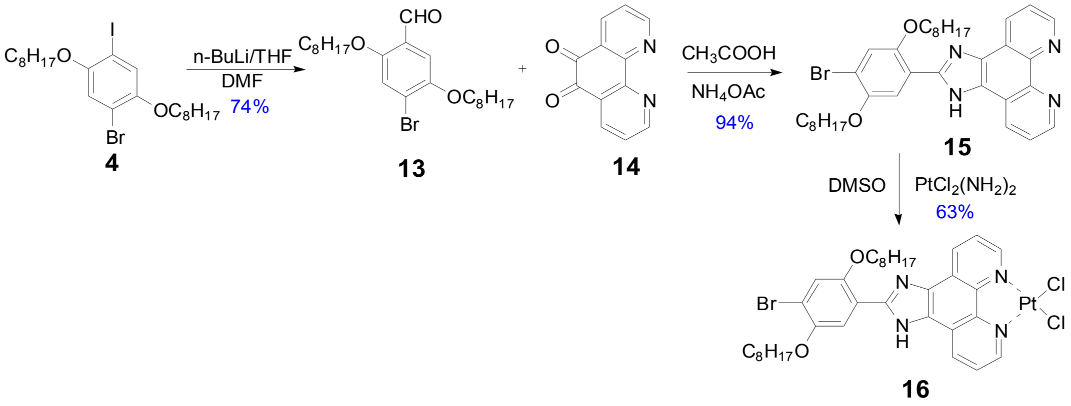
Results and discussion

Molecular design

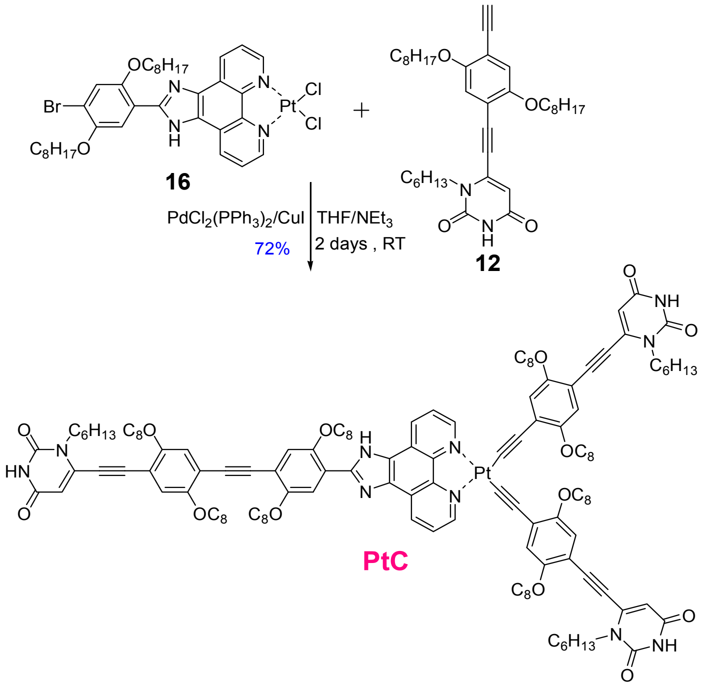
It is expected that fine tuning of counter H-bonded units having a central metal core and triple terminal dendritic units could be an ideal choice to realize entrenched electron/energy transfers via branching units offered by tetrapod structures. Derivative 12 containing both terminal alkyne and uracil H-bonded units was synthesized from compound 1 using a modular multi-step synthetic approach as shown in Scheme 1. 2-(4-Bromo-2,5-bis-octyloxy-phenyl)-1H-1,3,7,8-tetraaza cyclopenta[l]phenanthrene platinum dichloride (derivative 16) was prepared starting from aldehyde 13 and phenonthroline diketone 14 by using an acid catalysed imidazole formation, which was coupled with PtCl$_2$(NH$_2$)$_2$ under reflux in DMSO solution (see Scheme 2).[25] Furthermore, a central platinum core (**PtC**) containing peripheral uracil H-bonded units was synthesized using compounds 12 and 16 via sonogashira coupling strategy as depicted in Scheme 3. Platinum complex core was completely characterized by ^{1}H and ^{13}C NMR spectroscopies. Moreover, the abundant molecular ion peak in MALDI-TOF analysis affirmed the formation PtC as shown in Figure S1. Myriads of exceptional nano-material properties of dendrimers and supramolecular self-assemblies and our previous success in designing novel supramolecular architectures prompted us to accomplish the aforementioned task.[26] Dendrimers **TPAD1** and **TPAD2** were prepared according to our previous synthetic protocols.[27] With two counter H-bonded building moeties in hand to appreciate self-assembly properties further, we fabricated supramolecular H-bonded tetrads PtC-(**TPAD1**)$_3$ and **PtC**-(**TPAD2**)$_3$ via a classical supramolecular non-covalent H-bonded approach by our previous report as shown in Scheme 4.[27]

IR spectral studies

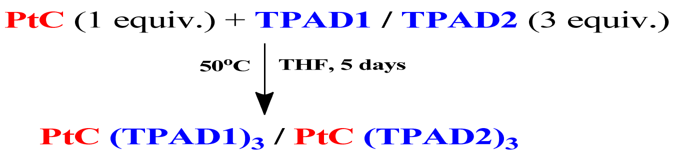
To probe the multiple H-bonded interactions between metal complex core (**PtC**) and dendritic H-bonded termini (**TPAD1** and



Scheme 2. Synthetic procedure of compound **16**.



Scheme 3. Synthetic procedure of **PtC**.



Scheme 4. Synthesis of H-bonded tetrads **PtC-(TPAD1)$_3$** and **PtC-(TPAD2)$_3$**.

TPAD2), attenuated total reflection fourier transform infrared (ATR-FTIR) measurements were carried out. As shown in Fig. 2, ATR-FTIR spectra of **TPAD1**, **TPAD2** and **PtC** in CH_2Cl_2 showed free NH stretching bands at 3438, 3420 and 3176 cm^{-1}, respectively. The NH stretching bands of supramolecular tetrads **PtC-(TPAD1)$_3$** and **PtC-(TPAD2)$_3$** (1:3 stoichiometry) in CH_2Cl_2 were observed at 3327 and 3328 cm^{-1}, respectively, which confirmed the formation of multiple H-bonding between the complementary H-bonded core (**PtC**) and dendrimers (**TPAD1** and **TPAD2**)[28] as noticed in Fig. 3.

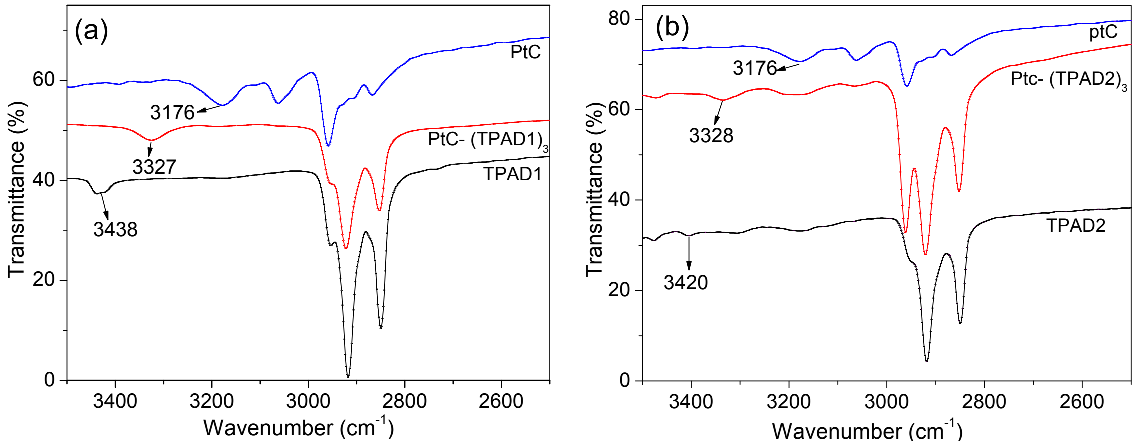


Fig. 2 ATR-FTIR spectra of H-bonded tetrads **PtC-(TPAD1)$_3$** and **PtC-(TPAD2)$_3$** in CH_2Cl_2 with 3:1 molar ratio of (a) **TPAD1** and **PtC** (b) **TPAD2** and **PtC**.

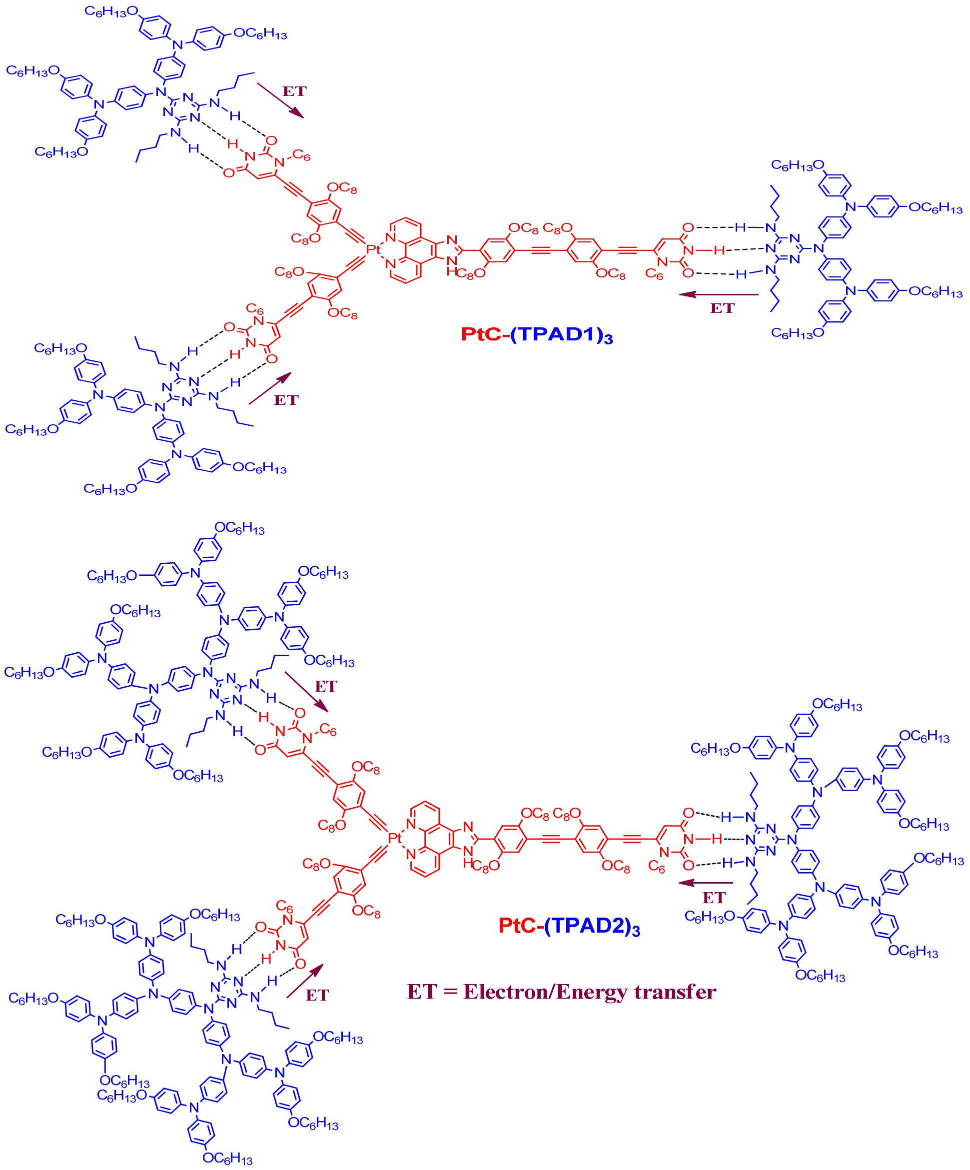


Fig. 3 Chemical structures of supramolecular tetrads **PtC-(TPAD1)$_3$** and **PtC-(TPAD2)$_3$** containing a platinum complex core (**PtC**) and two generations of H-bonded triarylamine dendrimers **TPAD1** and **TPAD2**, respectively.

^{1}H NMR titrations

To corroborate the presence of multiple H-bonds in tetrads further, we performed ^{1}H NMR titrations as shown in Fig. 4, in which **PtC** concentration was kept constant at 10 mM and the concentrations of dendrimers **TPAD1** and **TPAD2** were increased up to 3.5 equivalents with an equal span of 0.5 equivalent. While increasing the dendrimer concentrations in the range of 0-3.5 equivalents, the NH protons of **PtC** showed upfield shifts in both supramolecular tetrads from 11.08 to 9.71 ppm and from 11.08 to 9.65 ppm for PtC-(TPAD1)3 and PtC-(TPAD2)3, respectively. As noticed in Fig. 4, the downfield shifts of PtC-NH protons were also well evidenced for the formation of multiple H-bonds in the supramolecular complexes as per the literatures.[29] To further assess the multiple H-bonded interactions and the electron/energy transfer features between counter H-bonded moieties, we performed UV-Vis and PL titrations in chloroform solvent medium

UV-Vis and PL titrations

UV/Vis and PL titration experiments in chloroform were performed to study the interactions of both dendrimers (**TPAD1** and **TPAD2**) with metal complex core **PtC**. Upon adding aliquots of **TPAD1** to **PtC**, a bathochromic shift (Fig. 5a) from 408 to 413 nm was observed for the platinum complex absorption maximum corresponding to the S_0-S_1 electronic transition of **PtC-(TPAD1)$_3$**. A similar red-shift in **PtC-(TPAD2)$_3$**, i.e., from 408 to 415 nm (Fig. 5b), was observed during the UV/Vis titrations. During UV/Vis titrations, dendrimers **TPAD1** and **TPAD2** showed isosbestic points at 372 and 393 nm, respectively, which were arisen from the formation of multiple H-bonded tetrads in chloroform solutions. Simultaneously, the PL titrations of both supramolecular tetrads (Figs. 5c and 5d) showed bathochromic shifts in **PtC-(TPAD1)$_3$** (from 461 nm to 466 nm) and **PtC-(TPAD2)$_3$** (from 461 nm to 468 nm). Both results of UV/Vis and PL titrations verified that the metal complex core aggregations of **PtC** in both supramolecular tetrads. Similar to conventional *J*-aggregated dyes,[30] our supramolecular tetrads showed enhanced PL titrations during the formation of H-bonded structures, where the PL emission intensities of **PtC** were enhanced (λ_{ex}= 405 nm) by adding both dendrimers (**TPAD1** and **TPAD2** with electron-donating uniuts). This consequence was rationalized by an electron/energy-transfer process from the dendrimers **TPAD1** and **TPAD2** to the platinum complex core **PtC**. The observed UV/Vis and PL titration trends further confirmed a molar ratio of 1:3 as **PtC** H-bonded to both **TPAD1** and **TPAD2** to form supramolecular tetrads **PtC-(TPAD1)$_3$** and **PtC-(TPAD2)$_3$**, respectively.

TRPL spectra of energy transfers in H-bonded tetrads

To further evaluate the characteristics of energy transfers between H-bonded tetrads, we conducted TRPL measurements for both tetrads **PtC-TPAD1)$_3$** and **PtC-(TPAD2)$_3$**. Previous studies of metal-centered complexes revealed energy transfers arose from branched ends to metal centers.[31] Ventura et al. reported the energy transfer dynamics in multichromophoric arrays engineered from phosphorescent Pt(II)/Ru(II)/Os(II) centers linked to a central truxene platform.[32] They reported the electronic properties of the Ru and Os subunits in the arrays were found to be unaffected by the presence of the truxene core whereas direct linking of the Pt subunit to the truxene via the σ-alkyne bond markedly influenced the spectroscopic behavior of the Pt center as noticed by the TRPL studies (lifetime of 4.3 s for the mono ethynyl-bipy substituted truxene and 17.5 ms for the bis ethynyl-bipy substituted truxene). Therefore, the direct linking of uracil units in **PtC** through alkyne linkage would enhance energy transfers as evidenced by TRPL spectral studies. Similar to metal organic frameworks, multiple H-bonded assemblies demonstrated energy transfers as illustrated in previous reports.[33] Zhang et al. established the photoinduced electron transfer and charge-recombination in 2-ureido-4[1H]-pyrimidinone quadruple H-bonded porphyrin–fullerene assemblies which were also well

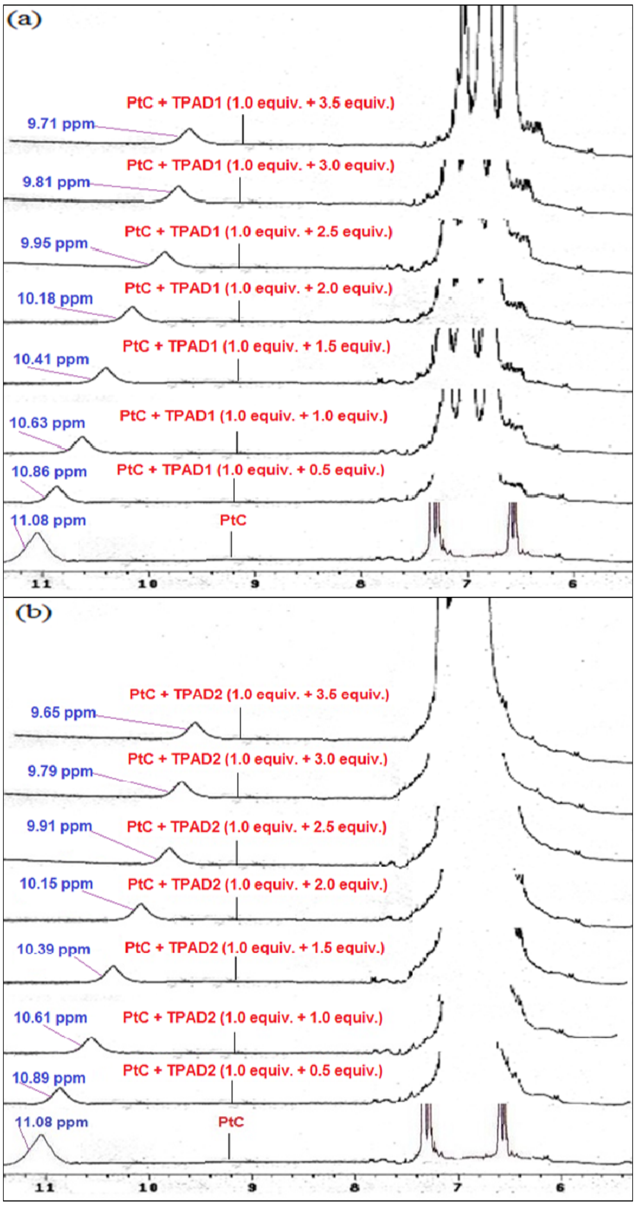


Fig. 4 ^{1}H NMR titrations of **PtC** with (a) **TPAD1** and (b) **TPAD2** (**PtC** was fixed at 1 equivalent and the concentrations of **TPAD1** and **TPAD2** were increased up to 3.5 equivalents with an equal span of 0.5 equivalent in d-chloroform).

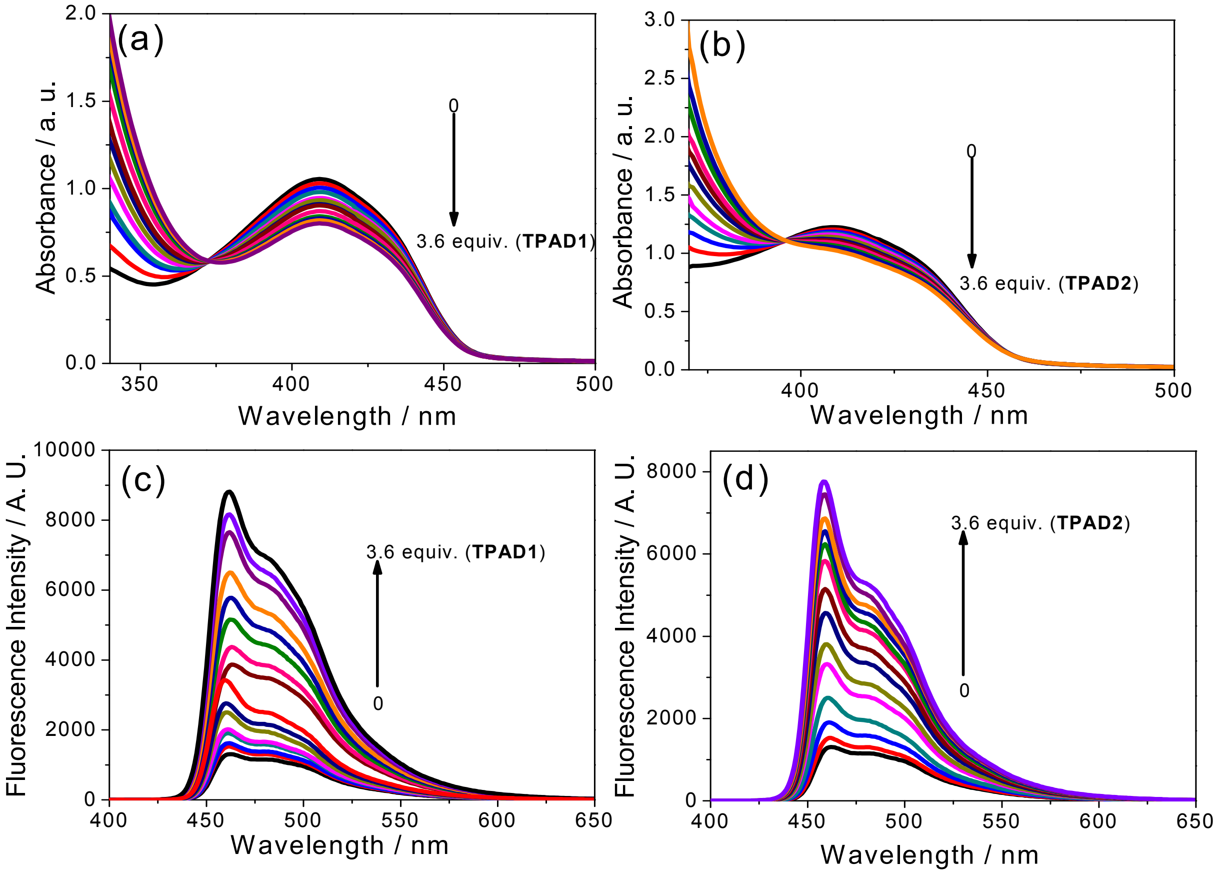


Fig. 5 UV-Vis and PL spectra of **PtC** upon titrations of (a, c) **TPAD1** and (b, d) **TPAD2** (**PtC** was fixed at 1 equivalent and the concentrations of **TPAD1** and **TPAD2** were increased up to 3.6 equivalents with an equal span of 0.3 equivalent in chloroform).

Recognized through time-resolved studies.[34] In addition, steady-state and time-resolved spectroscopies demonstrated that upon the excitation of the porphyrin, electron transfers to the fullerene occurred with rate constants of 1.6 × 10^8 s^{-1} (60%) and 4.2 × 10^8 s^{-1} (44%) for assemblies **I** and **II**, respectively, in a CH_2Cl_2 solution at room temperature. Therefore, the combination of both organic metal frame work and H-bonded assemblies would provide greater energy transfers as reported previously.[35] Hence we carried out TRPL studies as illustrated in Figs. 6a and 6b, the energy transfers occurred during tetrad formations of metal complex core **PtC** with various molar ratios of dendrimers (**TPAD1** and **TPAD2**) through TRPL spectral changes. As summarized in Table S1, we found that the fluorescence decay constants (τ) were affected typically by the energy transfers in both tetrads [**PtC-(TPAD1)$_3$** and **PtC-(TPAD2)$_3$**]. The average decay constants (τ_{avg}) of **PtC** were enhanced from 3.70 to 6.43 and 8.11 ns for **PtC-(TPAD1)$_3$** and **PtC-(TPAD2)$_3$**, respectively. The longer decay time values of H-bonded tetrads were attributed to the energy transfer contribution from complementary dendrimers, which appeared in the results of bi-exponential decay fittings. Similar to the changes of average decay constants (τ_{avg}), faster decay component (A_1) of **PtC** (28.3%) was increased to 45.2% and 47.1%, respectively, for both tetrads [**PtC-(TPAD1)$_3$** and **PtC-(TPAD2)$_3$**]. On the other hand, the longer decay component (A_2) of **PtC** (71.7%) was reduced to 54.8% and

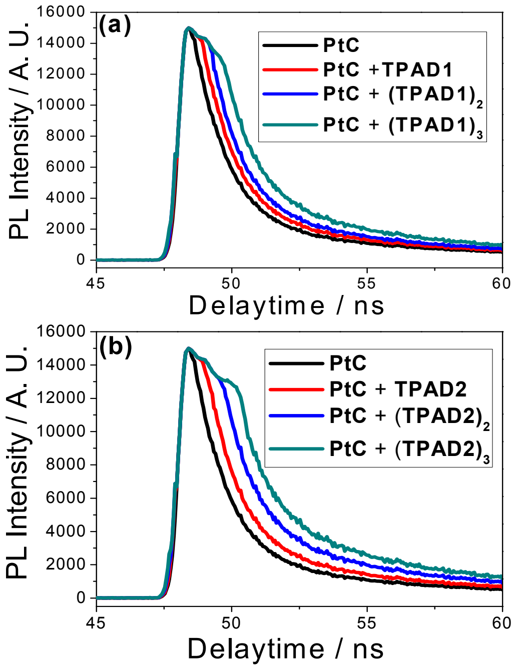


Fig. 6 (a) and (b) TRPL spectra of **PtC** with increasing concentrations of **TPAD1** and **TPAD2**, respectively. (0-3.0 equivs. with an equal span of 1 equiv.).

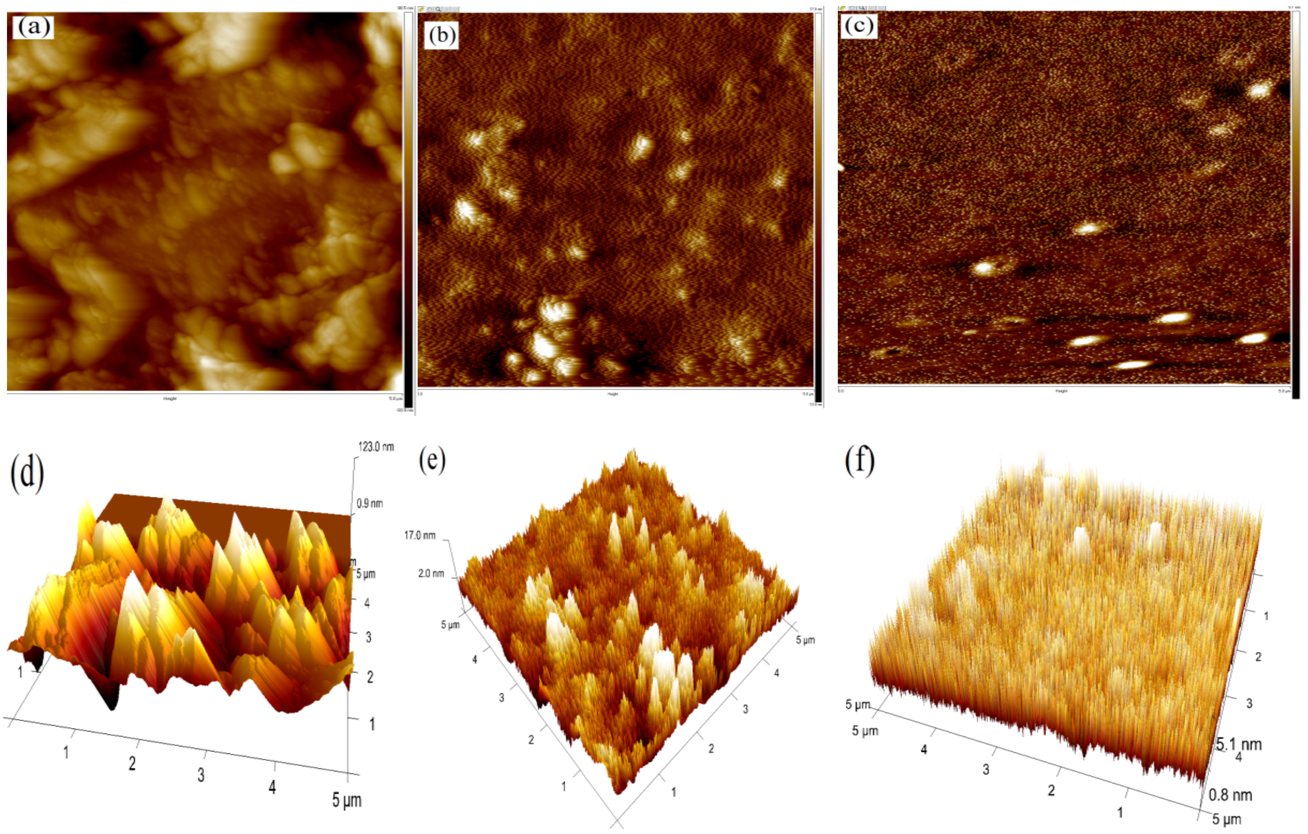


Fig. 7 AFM height and 3D images of (a, d) **PtC**, (b, e) **PtC-(TPAD1)$_3$**, (c, f) **PtC-(TPAD2)$_3$**, respectively. Scale bar 5 µM.

52.9%, respectively, for both tetrads [**PtC-(TPAD1)$_3$** and **PtC-(TPAD2)$_3$**], which also occurred in the chelations of Cu^{2+} and Ni^{2+} ions to our previous sensor polymers.[36] Due to *J*-aggregated assembly of both tetrads [**PtC-(TPAD1)$_3$** and **PtC-(TPAD2)$_3$**], the rapid changes in the life time of **PtC** were evidenced from the experimental data, which confirmed the electron/energy tranfers from triarylamine dendrimers (**TPAD1** and **TPAD2**) to platinum complex core (**PtC**) as noticed in Figs. 1 and 3. These results show that H-bonded assembles consisting of different kinds of building blocks, including platinum complex core (**PtC**) and two generations of triarylamine dendrimers (**TPAD1** and **TPAD2**), will become attractive for constructing supramolecular metallo-dendrimers by the self-assembly technique.

AFM studies

Encouraged by above studies in deducing the energy transfer features between counter H-bonded components, we further intrigued to investigate the morphological changes of these tetrads to understand self-assembly phenomena at nanoscale. Multiple H-bonded arrays have been shown to be versatile tools to prepare functional supramolecular materials in solutions. In this feature article, we report that the results obtained by designing and engineering a novel library of shape persistent molecular modules are able to transfer their geometrical information to the final supramolecular tetrad architectures through the formation of **PtC-(TPAD1)$_3$** and **PtC-(TPAD2)$_3$** complexes at the nanoscopic levels. Previously, Sun et. al. reported the morphology and chirality of the supercoils demonstrated photoresponsivities through AFM studies, which were induced from the photoisomerization of the azobenzene components within the self-assembled nanostructures.[37a] Similarly, the utility of an external structure-directing agent to induce orthogonal H-bonding-mediated programmed supramolecular-assembly via AFM analysis and gelation of an n-type NDI chromophore was reported by Ghosh et. al.[37b] Additionally, many reports evidenced the presence of multiple H-bonds have provided self-assemblies with nano-level aggregations.[37] As shown in Fig. 7, atomic force microscpy (AFM) images of metal complex core **PtC** and both generations of tetrads were measured and investigated. Upon H-bonded with metal complex core **PtC**, the roughnesses of tetrads **PtC-(TPAD1)$_3$** and **PtC-(TPAD2)$_3$** were reduced to different extents due to their self-assemblies, where the roughnesses of **PtC**, **PtC-(TPAD1)$_3$** and **PtC-(TPAD2)$_3$** were around 123 nm, 17 nm and 5.1 nm, respectively. Hence, it also confirmed the self-assemblies provided different degrees of uniform aggregations in two generations of tetrads to enhance the electron/energy transfers.

Sensor properties of PtC

Due to the excellent photophysical properties, **PtC** (0.1 µM) in THF was initially investigated towards 1000 µM of metal ions (Li^+, Ag^+, K^+, Na^+, Cs^+, Ni^{2+}, Fe^{3+}, Co^{2+}, Zn^{2+}, Cd^{2+},Pb^{2+}, Ca^{2+}, Cr^{3+}, Mg^{2+}, Cu^{2+}, Mn^{2+}, Hg^{2+}, Fe^{2+} and Ag^{2+}) in H_2O. As noticed in Figs. 8 and 9, **PtC** showed a better selectivity towards Ag^+, whereas other metal ions showed negligible sensitivities to **PtC**. Sensor selectivity of **PtC** towards Ag^+ was further confirmed by single and dual metal analysis as Follows: During single metal analysis of **PtC** shown in Fig. 8, Ag^+ provided a huge fluorescence quenching in **PtC** + Ag^+, where the PL intensity (I = 261 at 461 nm for **PtC** + Ag^+) was 36-fold reduced in contrast to **PtC** (I_0 = 9694 at 461 nm), and all other metal ions exhibited trivial responses. Similarly, the greater selectivity of **PtC** towards Ag^+ (1000 µM) in the presence of other metal ions (1000 µM) was evidenced in the background metal analysis of **PtC** as noticed in Fig. S2. In both cases sensor selectivity of **PtC** towards Ag^+ was further confirmed by stern-volmer quenching constant values as summarized in Table S2. Stern-volmer quenching constant (K_{SV}) of **PtC**+Ag^+ was found to be 3.61 x 10^4/mol and other metal ions are in the range of 10^2/mol.

Sensor titration of PtC with Ag^+

Upon titration of **PtC** (0.1 µM) with Ag^+ (0-1000 µM with an equal span of 100 µM in H_2O), the PL intensity of **PtC** at 461 nm was quenched slowly as noticed in Fig. 10. Similarly, PL quenching of **PtC** was well established in Fig. S3 and the detection limit of Ag^+ by **PtC** was calculated as 5.54 x 10^5 M by standard deviation and linear fittings as shown in Fig. S4. The linear fluorescent quenching of **PtC** upon the addition of Ag^+ ions, may arise from the binding of Ag^+ with imidazole unit of **PtC**. However, to confirm the above assumption we extended our investigation by NMR titration of **PtC** with Ag^+ to establish the binding site as listed below.

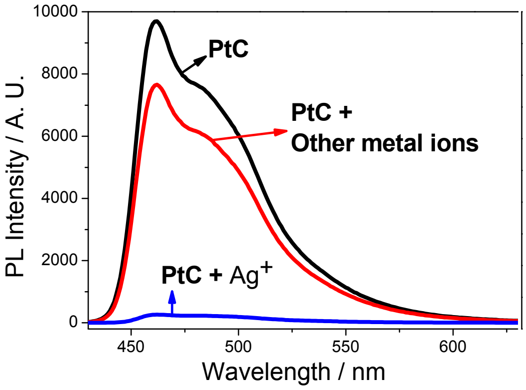


Fig. 8 Sensor selectivity of **PtC** (i.e., responses of PL intensities at 461 nm) towards various metal ions; where **PtC** concentration is 0.1 µM and the metal ion concentration is 1000 µM. (λ_{ex} = 405 nm & λ_{em} = 461 nm).

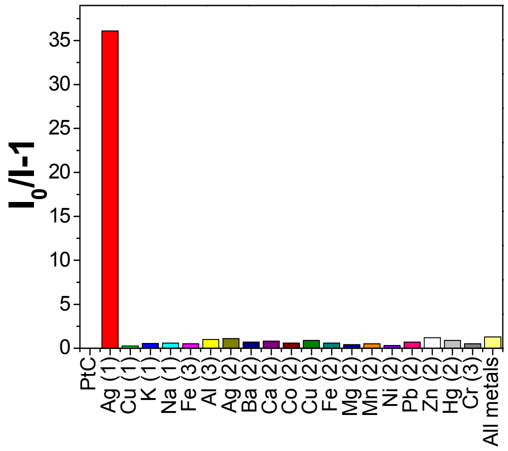


Fig. 9 **PtC** sensor selectivity towards metal ions (I_0: initial PL intensity of **PtC**; I: PL intensity of **PtC** with metal ions); where **PtC** concentration is 0.1 µM and the metal ion concentration is 1000 µM.

Stoichiometry and binding site of PtC+Ag^+

In general, the stoichiometry tests of sensor complexes could give us a clear idea of their binding sites. However, due to the low concentration usage of **PtC** (0.1 µM) in the sensor titration with higher concentrations of Ag^+ (0-1000 µM with an equal span of 100 µM), the stoichiometry of **PtC**+Ag^+ was not calculated from UV/PL titrations. Hence, to calculate the stoichiometry and binding site of **PtC**+Ag^+ the ^{1}H NMR titration was carried out as shown in Figure 11. The ^{1}H NMR titration of **PtC** in d_8-THF (10 mmol) with Ag^+ in D_2O (0-10 mmol with an equal span of 2

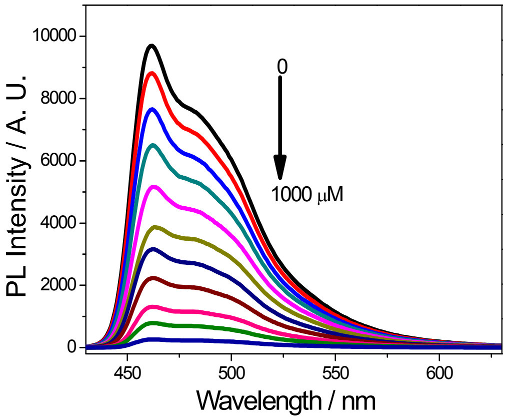


Fig. 10 PL titration of **PtC** (0.1 µM) with Ag^+ (0-1000 µM) by increasing concentration with an equal span of 100 µM.

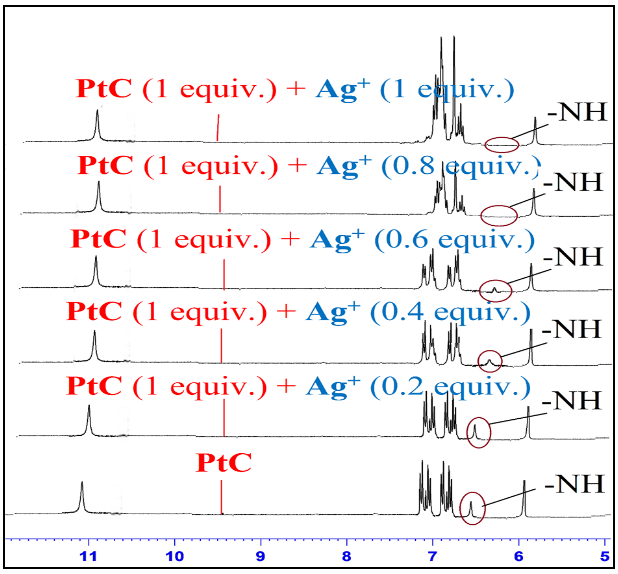


Fig. 11 ^{1}H NMR titration of **PtC** (10 mmol in d_8-THF) with Ag^+ by increasing concentration (0-10 mmol) with an equal span of 2 mmol in D_2O.

mmol) established the stoichiometry and binding site towards the sensor response. Interestingly, the -NH peak of imidazole group in **PtC** diminished slowly with increasing concentration of Ag^+ in D_2O. However, the remaining ^1H NMR peaks except -NH peak of imidazole moiety were not affected as noticed in Fig. 11. Moreover, the ^1H NMR titration of **PtC** with Ag^+ also confirmed the 1:1 stoichiometry of **PtC**+Ag^+ as well. Since the -NH imidazole peak of **PtC** was not affected after 0.8 equiv. addition of Ag^+ in D_2O, the 1:1 stoichiometry of **PtC**+Ag^+ was further proven. Similarly, the binding site of **PtC**+Ag^+ was further verified by the reversibility test of **PtC**+Ag^+ through the addition of few drops of PMDTA in THF.[38] As noticed in Fig. S5, fluorescence emission of **PtC** was restored upon the addition of PMDTA, hence the dissociation of complex **PtC**+Ag^+ was proven by the reversibility test of **PtC**+Ag^+. On the other hand, the photograph of sensor reversibility of **PtC**+Ag^+ upon the addition of PMDTA also supported the same idea as shown in Fig. 12. Therefore, a possible binding mechanism of **PtC** towards Ag^+ was proposed as noticed in Fig. S6. However, to further confirm the imidazole binding site, we made attempts to carry out the sensor titrations with compounds **15** and **16**. Nevertheless, because of multiple binding sites in **15** (two phenonthroline nitrogens) and low solubility of **16** in THF, we were unable to obtain their sensor properties from both compounds. As reported in the literature and from our previous results[39] (Fig. S7), we found that the fluorescence decay constants (τ) were affected typically by turn-off sensor responses as summarized in Table S1. From the TRPL signals without any sensor responses the fluorescence life time values of **PtC** were reduced from 3.70 ns to 2.95 ns. During the sensing process of **PtC**+Ag^+, a faster decay component (A_1) of **PtC** (28.3%) was increased to 76.2%, along with 71.7% of a longer decay component (A_2) was reduced to 23.8% as shown in Table S1.

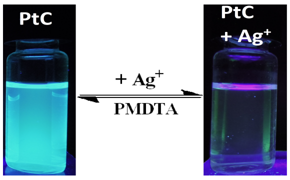


Fig. 12 Photographs of titrations of **PtC** with reversible (on-off-on) fluorescence changes towards Ag^+ and its reversibility upon a further addition of PMDTA. (under UV lamp with λ_{ex} = 365 nm & λ_{em} = 461 nm).

Conclusions

In this study, we designed and synthesized a novel metal complex **PtC** possessing a central platinum core and three terminal uracil H-bonded units via a modular synthetic approach. For the first time, **PtC** complex was successfully synthesized to be utilized as a selective sensor probe towards Ag^+ recognition and to be self-assembled with two complimentary dendrimers **TPAD1** and **TPAD2** to form novel H-bonded tetrads **PtC-(TPAD1)$_3$** and **PtC-(TPAD2)$_3$**, respectively. The existence and preservance of multiple H-bonds in both tetrads were demonstrated by ^1H NMR titration, as well as IR and TRPL spectral studies. Furthermore, electron/energy trasfer features in these tetrads were established by UV-Vis and PL titrations of **PtC** with two generations of dendrimers **TPAD1** and **TPAD2** with electron-donating units. Self-assembled nanostructural formation with smoother surface roughness in tetrads compared to its precursors in AFM studies further affirmed self-assembly at nanoscale. Exclusively, the **PtC** core showed a better selective and sensitive metal rocignition capbility towards Ag^+ without interfering from commonly encountered transition metals. The 1:1 stoichimetry of Ag+ complex formed during the sensing event was established by ^1H NMR trtratio profiles. Remarkably, the on-off-on reversible etiqutte formation by Ag+ and PMDTA was successfully achieved. Thus, we believe that the current findings in this study would certaintly illuminate the field of metal complexed nano-self-assembled structures. Furthermore, opto-electronic applications of these H-bonded tetrads are currently underway in our laboratory.

Experimental

Materials and methods

All anhydrous reactions were carried out by standard procedures under nitrogen atmosphere to avoid moisture, and all solvents were dried by distillation over appropriate drying agents. Reactions were monitored by TLC plates and column chromatography was generally performed on silica gel. ^1H and ^{13}C NMR spectra were recorded on a 300 MHz spectrometer. The chemical shifts (δ) in ppm and coupling constants (*J*) in Hz were obtained relative to TMS (0.00) and d-chloroform (7.26 & 77.0) for ^1H and ^{13}C NMR spectra (s, d, t, q, m and br means single, double, ternary, quadruple, multiple and broad single, respectively). Mass spectra (MALDI and FAB) were acquired on the respective mass spectrometers. Elemental analysis was carried out by Elemental Vario EL. ATR-FTIR spectra were measured by using Perkin Elmer spectrum 100 series spectrometer, which were collected at a resolution of 4 cm^{-1} using a deuterated triglycine sulfate detector by averaging four scans. Absorption and fluorescence spectra were measured on V-670 Spectrophotometer and F-4500 Fluorescence Spectrophotometer, respectively. Identification and purity of the Intermediates were characterized by NMR (^1H & ^{13}C), Mass (MALDI and FAB) and melting point measurements. Whereas the synthesis of final dendrimers **TPAD1** and **TPAD2** were synthesized as reported previously.[27] Compounds **TPAD1**, **TPAD2** and **PtC** were dissolved in $CHCl_3$ at 1 x 10^{-5} M, for UV/Vis and PL titrations. Both tetrads **PtC-(TPAD1)$_3$** and **PtC-(TPAD2)$_3$**, obtained from Scheme 4, were dissolved in $CHCl_3$ and their solid films were prepared by spin coating and then measured. Time-resolved photoluminescence (TRPL) spectra were measured using a home-built single photon counting system. Excitation was performed using a 450 nm diode laser (Picoquant PDL-200, 50 ps fwhm, 2 MHz). The signals collected at the excitonic emissions of solutions were connected to a time-correlated single photon counting card (TCSPC, Picoquant Timeharp 200). The emission decay data were analyzed with the biexponential kinetics in which two decay components were derived. The lifetime values (τ_1 and τ_2) and pre-exponential factors (A_1 and A_2) were determined and summarized. Li^+, Ag^+, K^+, Na^+, Cs^+, Ni^{2+}, Fe^{3+}, Co^{2+}, Zn^{2+}, Cd^{2+},Pb^{2+}, Ca^{2+}, Cr^{3+}, Mg^{2+}, Cu^{2+}, Mn^{2+}, Hg^{2+}, Fe^{2+} and Ag^{2+} metal ions were dissolved in water medium at 1 x 10^{-3} M concentration from their respective chloro compounds and **PtC** was dissolved in THF medium at 1 x 10^{-7} M concentration.

Synthesis of *1,4-bis-octyloxy-benzene* (2)

To a 500 ml flask containing 10 g (9 mmol) of hydroquinone (**1**) in 200 ml of DMF, 37 ml (22.5 mmol; 2.5 equiv.) of 1-bromohexane was added and refluxed for 36 hrs under N_2 atmosphere. Then, the mixture was cooled to room temperature and water was added. The precipitate was filtered and dried in vacuo for 3 hrs, then recrystallized with ethanol to afford the pure compound. Yield: 28.86 g (95%); ^{1}H NMR (300 MHz, $CDCl_3$): 6.82 (s, 4H), 3.90 (t, J = 6.0 Hz, 4H), 1.74-1.65 (m, 4H), 1.34-1.27 (m, 20H), 0.88 (t, J = 6.6 Hz, 6H).

Synthesis of *2-bromo-1,4-bis-octyloxy-benzene* (3)

10 g (29.9 mmol) of compound **2** was dissolved in 100 ml of CH_3CN in a 250 ml flask under N_2 atmosphere. 5.5 g (32.9 mmol; 1.1 equiv.) of N-bromosuccinimide (NBS) was added portionwise and stirred for 24 hrs. Excess solvent was distilled out. The crude product was purified by column (SiO_2) by 99:1 hexane:EtOAc to afford a colorless oil. Yield: 10.26 g (83%); ^{1}H NMR (300 MHz, $CDCl_3$): 7.12 (s, 1H), 6.80 (s, 2H), 3.95 (t, J = 6.0 Hz, 2H), 3.88 (t, J = 6.0 Hz, 2H), 1.83-1.72 (m, 4H), 1.30-1.49 (m, 20H), 0.88 (t, J = 6.6 Hz, 6H).

Synthesis of *1-bromo-4-iodo-2,5-bis-octyloxy-benzene* (4)

5 g (12.1 mol) of compound **3** was dissolved in CH_3COOH:H_2O:conc.H_2SO_4 (95:3:2) mixture and heated to 80°C for 30 minutes. Cooled to 50°C, 1.3 g (0.78 mmol) of KI and 0.91 g (0.43 mmol) of KIO_3 was added and refluxed at 80°C for 24 hrs. After cooled to room temperature, the mixture was quenched with Na_2SO_4 and then extracted with hexane. The pure compound **4** was obtained by column chromatography (SiO_2) 99:1 hexane:EtOAc to afford a white solid. Yield: 5.94 g (91%); ^{1}H NMR (300 MHz, $CDCl_3$): 7.26 (s, 1H), 6.96 (s, 1H), 3.92 (t, J = 6.0 Hz, 4H), 1.82-1.76 (m, 4H), 1.34-1.48 (m, 20H), 0.89 (t, J = 6.0 Hz, 6H).

Synthesis of *4-bromo-2,5-bis-octyloxy-phenylethynyl)-trimethyl-silane* (5)

To a 5 g (9.3 mmol) of compound **4** in a 250 ml flask purged with continuous N_2 atmosphere, 39 mg (0.05 mmol) of $PdCl_2(PPh_3)_2$ and CuI (0.05 mmol) were added with constant stirring. Then, 5 ml of freshly distilled THF was added via syringe and stirred for 10 minutes. Thereafter, Et_3N 45 ml was added and then heated to 50°C. 1.32 ml (9.3 mmol; 1 equiv.) of TMSA was added and refluxed at 50°C for 12 hrs and monitored via TLC. After completion, the mixture was cooled to RT, and the excess solvent was quenched and distilled out. The product was purified through column (SiO_2) 9:1 hexane:EtOAc to afford a yellow solid. Yield: 4.63 g (98%); ^{1}H NMR (300 MHz, $CDCl_3$): 7.08 (s, 1H), 6.94 (s, 1H), 3.94 (t, J = 6.0 Hz, 4H), 1.81-1.74 (m, 4H), 1.49-1.29 (m, 20H), 0.89 (t, J = 6.0 Hz, 6H), 0.25 (s, 9H).

Synthesis of *1-bromo-4-ethynyl-2,5-bis-octyloxy-benzene* (6)

4.5 g of compound **5** was dissolved in THF with 2 drops of water with constant stirring, and then a few drops of tetrabutyl ammonium fluoride (TBAF) was added and stirred for 3 hrs. Monitored by TLC, upon completion of the reaction, the solvent was distilled out and purified through column (SiO_2) 9:1 hexane:EtOAc to afford a yellow solid, which was proceeded for the next step immediately. Yield: 3.83 g (99%); ^{1}H NMR (300 MHz, $CDCl_3$): 7.07 (s, 1H), 6.96 (s, 1H), 3.96 (t, J = 6.0 Hz, 4H), 3.28 (s, 1H), 1.84-1.74 (m, 4H), 1.46-1.28 (m, 20H), 0.88 (t, J = 6.0 Hz, 6H).

Synthesis of *1-hexyluracil* (8)

K_2CO_3 (14.80 g, 107.05 mmol) was added to a suspension of uracil (10.0 g, 89.21 mmol) in DMSO (150 mL) and stirred for 15-20 min at 45°C. 1-Bromohexane (3.5 mL, 25 mmol) was added and the reaction mixture was stirred for 48 hrs. The reaction was cooled to room temperature and poured into cold water. The product was extracted three times with DCM, and washed with dilute HCl, water, brine, and dried over Mg_2SO_4. The organic layer was concentrated and poured into cold hexane with vigorous stirring. The resulting precipitate was filtered and washed with cold hexane to afford compound **8** (17.88 g, 69%) as a white solid.^{1}H NMR (300 MHz, $CDCl_3$): 9.12 (br, 1H), 7.14 (d, J = 9.0 Hz, 1H), 5.70 (d, J = 6.0 Hz, 1H), 3.71 (t, J = 7.5 Hz, 2H), 1.68-1.64 (m, 2H), 1.30-1.28 (m, 6H), 0.87 (t, J = 6.6 Hz, 3H).

Synthesis of *1-hexyl-6-iodouracil* (9)

At 78°C, LDA (20.4 mL of a 2.5 M solution, 51.0 mmol) was added drop wise to a solution of 1-hexyluracil (2.0 g, 10.2 mmol) in THF (55 mL), and the resulting solution was stirred under N_2 for 2 hrs. I_2 (12.9 g, 51.0 mmol) was added and the reaction mixture was stirred for another 2 h at the same temperature. Acetic acid (2.0 mL) was added to react with stirring at room temperature for overnight. The organic phase was extracted with ethyl acetate and washed with saturated $NaHCO_3$ (3 x 30.0 mL) and Na_2SO_3 (3 x 30 mL) solutions. Finally, the product was washed with brine (30 mL) and dried over Mg_2SO_4. The solvent was removed by rotary evaporator and the crude product was purified by column chromatography silica (hexane:ethyl acetate = 5:5) to afford compound **9** (2.2 g, 67%).^{1}H NMR (300 MHz, $CDCl_3$): 9.48 (br, 1H), 6.41 (s, 1H), 4.0 (t, J = 8.1 Hz, 2H), 1.69-1.64 (m, 2H), 1.37-1.32 (m, 6H), 0.88 (t, J = 6.9 Hz, 3H).

Synthesis of *6-(4-bromo-2,5-bis-octyloxy-phenylethynyl)-1-hexyl-1H-pyrimidine-2,4-dione* (10)

To a mixture of compound **9** (1.26 g, 3.9 mmol) in THF (15 mL), 1-bromo-4-ethynyl-2,5-bis-octyloxy-benzene (**6**) (2.0 g, 3.9 mmol), CuI (10 mg, 0.05 mmol) and NEt_3 (15 mL) were added. Then, $[Pd(PPh_3)_2\ Cl_2]$ (4 mg, 0.034 mmol) was added under N_2 and the reaction mixture was heated to 50°C for 36 hrs. The crude product was extracted with DCM followed by brine wash and dried over Mg_2SO_4. The resulting solution was concentrated by rotary evaporator, and purified by column chromatography using silica, (hexane: ethyl acetate=7:3) to give a yellow solid. (1.98 g, yield 58%). ^{1}H NMR (300 MHz, $CDCl_3$): 9.32 (br, 1H), 7.12 (s, 1H), 6.93 (s, 1H), 5.98 (s, 1H) 4.0 (t, J = 6.1 Hz, 2H), 3.96 (t, J = 7.5 Hz, 4 H), 1.86-1.69 (m, 6H), 1.48-1.27 (m, 26H), 0.88 (t, J = 6.9 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): 162.9, 155.2, 151.0, 149.6, 139.2, 117.7, 117.5, 116.9, 109.1, 106.5, 97.4, 84.8, 70.4, 69.7, 46.8, 32.0, 31.7, 29.5, 29.3, 29.1, 26.5, 26.2, 26.1, 22.9, 22.7, 14.3, 14.2; (FAB) calculated:630.30; found: 630.30.

Synthesis of *6-(2,5-bis-octyloxy-4-trimethylsilanylethynyl-phenylethynyl)-1-hexyl-1H- pyrimidine-2,4-dione* (11)

Compound **11** was synthesized as per the synthetic procedure of compound **5** with a final 89 % yield; ^{1}H NMR (300 MHz, CDCl$_3$): 9.32 (br, 1H), 7.12 (s, 1H), 6.93 (s, 1H), 5.98 (s, 1H) 4.0 (t, *J* = 6.1 Hz, 2H), 3.96 (t, *J* = 7.5 Hz, 4 H), 1.86-1.69 (m, 6H), 1.48-1.27 (m, 26H), 0.88 (t, *J* = 6.9 Hz, 9H), 0.12 (s, 9H); ^{13}C NMR (75 MHz, CDCl$_3$): 162.9, 155.2, 151.0, 149.6, 139.2, 117.7, 117.5, 116.9, 109.1, 106.5, 99.3, 99.0, 97.4, 84.8, 70.4, 69.7, 46.8, 32.0, 31.7, 29.5, 29.3, 29.1, 26.5, 26.2, 26.1, 22.9, 22.7, 15.7, 14.3, 14.2, 0. 17; (FAB) calculated:648.43; found: 648.43.

Synthesis of *6-(4-ethynyl-2,5-bis-octyloxy-phenylethynyl)-1-hexyl-1H-pyrimidine-2,4-dione* (12)

Compound **12** was synthesized as per the synthetic procedure of compound **6** with a final 89 % yield; ^{1}H NMR (300 MHz, CDCl$_3$): 9.32 (br, 1H), 7.12 (s, 1H), 6.93 (s, 1H), 5.98 (s, 1H) 4.0 (t, *J* = 6.1 Hz, 2H), 3.96 (t, *J* = 7.5 Hz, 4 H), 3.31 (s, 1H), 1.84-1.74 (m, 6H), 1.46-1.28 (m, 26H), 0.88 (t, *J* = 6.9 Hz, 9H); ^{13}C NMR (75 MHz, CDCl$_3$): 162.9, 155.2, 151.0, 149.6, 139.2, 117.7, 117.5, 116.9, 109.1, 106.5, 99.3, 99.0, 97.4, 84.8, 81.8, 79.5, 70.4, 69.7, 46.8, 32.0, 31.7, 29.5, 29.3, 29.1, 26.5, 26.2, 26.1, 22.9, 22.8, 14.3, 14.2; ; (FAB) calculated: 576.39; Found: 576.39; Elemental analysis; calculated: C, 74.96; H, 9.09; N, 4.86, found: C, 74.67; H, 9.06, N, 4.88.

Synthesis of *4-bromo-2,5-bis-octyloxy-benzaldehyde* (13)

5 g of compound **6** in 50 ml THF was stirred under N$_2$ atm and cooled to -78°C maintained for 1 hr. To the solution, 1 equiv. of n-BuLi was added, then temperature was raised to 0°C; 1 equiv. of DMF was added and stirred for 12 hrs at RT. Excess n-BuLi was quenched with 2 drops of HCl and the solvent was distilled out. Finally, a pure compound was obtained via column (SiO$_2$) 9:1 hexane:EtOAc to afford a yellow solid. Yield: 3.03 g (74%); ^{1}H NMR (300 MHz, CDCl$_3$): 10.40 (s, 1H), 7.29 (s, 1H), 7.21 (s, 1H), 3.99 (t, *J* = 6.0 Hz, 4H), 1.84-1.74 (m, 4H), 1.46-1.28 (m, 20H), 0.88 (t, J = 6.0 Hz, 6H).

Synthesis of *2-(4-bromo-2,5-bis-octyloxy-phenyl)-1H-1,3,7,8-tetraaza-cyclopenta[l]- phenanthrene* (15)

1:1 mixture of aldehyde (**11**) and phenonthroline diketone (**14**) was dissolved completely in acetic acid. To that solution excess (30 equiv.) of NH$_4$OAc was added and refluxed for 12 hrs. The product formation was monitored by TLC. After completion the crude product was recrystallized from absolute ethanol to afford compound **15** with 94 % yield; ^{1}H NMR (300 MHz, CDCl$_3$): 11.13 (s, 1H), 9.05 (s, 2H), 8.85 (d, 1H), 7.92 (s, 2H), 7.49-7.60 (m, 2H), 7.07 (s, 1H), 4.08 (t, *J*= 6 Hz, 2H) 3.99 (t, *J* = 6.1 Hz, 2H), 1.84-1.74 (m, 4H), 1.46-1.28 (m, 20H), 0.88 (t, *J* = 6.9 Hz, 6H); ^{13}C NMR (75 MHz, CDCl$_3$): 150.5, 149.8, 148.7, 148.3, 148.2, 135.7, 130.5, 127.9, 124.7, 124.5, 123.3, 122.7, 118.7, 117.8, 117.1, 114.3, 112.7, 70.2, 60.9, 32.1, 29.8, 29.7, 29.6, 29.5, 26.7, 26.3, 22.9, 22.7, 14.4, 14.2; (FAB) calculated: 630.3; found: 630.3; Elemental analysis; calculated: C, 66.55; H, 6.86; N, 8.87, found: C, 66.57; H, 6.81, N, 8.88.

Synthesis of *2-(4-bromo-2,5-bis-octyloxy-phenyl)-1H-1,3,7,8-tetraaza-cyclopenta[l]phenanthrene platinum dichloride* (16)

1:1 mixture of compound **15** and PtCl$_2$(NH$_2$)$_2$ was dissolved completely in DMSO and refluxed at 100°C for 12 hrs to afford yellow solid of compound **16**. The solid was filtered off and washed with excess water and dried over vacuum at 70°C for 6 hrs. Yield: 63%; ^{1}H NMR (300 MHz, CDCl$_3$): 11.13 (br, s, 1H), 9.02 (br, s, 2H), 8.78 (br, s, 2H), 8.49 (br, s, 2H), 7.31-7.55 (br, m, 2H), 6.76 (br, s, 1H), 4.08 (br, t, 2H) 3.96 (br, t, 2H), 1.79-1.26 (br, m, 24H), 0.91 (br, t, 6H); (FAB) calculated: 897.63; found: 897.63.

Synthesis of *PtC*

To a mixture of compound **16** (1 equiv.) in THF (15 mL), 6-(4-ethynyl-2,5-bis-octyloxy-phenylethynyl)-1-hexyl-1H-pyrimidine-2,4-dione (**6**) (10 equiv.), CuI (0.1 equiv.) and NEt$_3$ (15 mL) were added. Then, PdCl$_2$(PPh$_3$)$_2$ (1 equiv.) was added under N$_2$ and the reaction mixture was stirred at room temperature for 48 hrs. The crude product was extracted with DCM followed by brine wash and dried over Mg$_2$SO$_4$. The resulting solution was concentrated by rotary evaporator, and purified by column chromatography using neutral alumina, (CH$_2$Cl$_2$:MeOH=9:1) to give a yellow solid. Yield: 72%; ^{1}H NMR (300 MHz, CDCl$_3$): 11.08 (s, 3H(NH)), 7.12 (m, 7H), 6.83 (m, 7H), 6.61 (s, 1H (NH)), 5.98 (s, 3H) 4.09 (t, *J* = 6.1 Hz, 6H), 3.96 (t, *J* = 7.5 Hz, 16H), 1.84-1.74 (m, 24H), 1.46-1.28 (m, 96H), 0.88 (t, *J* = 6.9 Hz, 33H); ^{13}C NMR (75 MHz, CDCl$_3$): 162.5, 155.2, 151.0, 149.6, 139.2, 130.5, 127.8, 124.7, 124.2, 123.3, 122.7, 118.7, 117.7, 117.1, 114.3, 112.7, 109.1, 106.5, 99.3, 99.0, 97.4, 84.8, 81.8, 70.4, 69.7, 46.8, 32.0, 31.7, 29.5, 29.3, 29.1, 26.5, 26.2, 26.1, 22.9, 22.7, 14.3, 14.2; Maldi-Tof; calculated: 2473.24, found: 2473.24; Elemental analysis; calculated: C, 69.42; H, 7.98; N, 5.66, found: C, 68.57; H, 7.76, N, 5.58.

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Table of Contents (TOC)/ABSTRACT Graphic

A novel metal complex **PtC** possessing central platinum core and three terminal uracil H-bonded units via a modular synthetic approach was designed and synthesized. For the first time, **PtC** core was successfully utilized in both self-assembly formation of H-bonded tetrads with two generations of dendrimers (**TPAD1** and **TPAD2**) and as a selective sensor for the recognition of Ag^+.