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Metallacycle-Cored Supramolecular Polymers: Fluorescence Tuning by Variation of Substituents

Luonan Xu[†], Xi Shen[†], Zhixuan Zhou[‡], Tian He[†], Jinjin Zhang[†], Huayu Qiu[†], Manik Lal Saha[‡], Shouchun Yin^{*,†,‡}, and Peter J. Stang^{*,‡}

[†]College of Material, Chemistry and Chemical Engineering, Hangzhou Normal University, Hangzhou 310036, P. R. China

[‡]Department of Chemistry, University of Utah, 315 South 1400 East, Room 2020, Salt Lake City, Utah 84112, United States

Abstract

Herein, we present a method for the preparation of supramolecular polymers with tunable fluorescence via the combination of metal-ligand coordination and phenanthrene-21-crown-7(P21C7)- based host-guest interaction. A suite of rhomboidal metallacycles with different substituents were prepared via the coordination-driven self-assembly of a P21C7- based 60° diplatinum (II) acceptor and 120° dipyridyl donors. By the variation of the substituents on the dipyridyl donors, the metallacycles exhibit emission wavelengths spanning the visible region ($\lambda_{\text{max}} = 427\text{--}593\text{ nm}$). Metallacycle-cored supramolecular polymers were obtained via host-guest interactions between bisammonium salts and P21C7. The supramolecular polymers exhibit similar emission wavelengths of the individual metallacycles and higher fluorescent efficiency in solution and thin films. Utilizing a yellow-emitting supramolecular polymer thin film with high quantum yield (0.22), a white-light-emitting LED was fabricated by painting the thin film onto an ultra violet-LED. This study presents an efficient approach for tuning the properties of fluorescent supramolecular polymers and potential of metallacycle-cored supramolecular polymers as a platform for the fabrication of light-emitting materials with good processability and tunability.

Table of Contents

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*yinsc@hznu.edu.cn

*stang@chem.utah.edu

ASSOCIATED CONTENT

Supporting Information

The supporting information is available free of charge via the Internet at <http://pubs.acs.org>.

Syntheses and characterization data (NMR, ESI-TOF-MS, Fluorescence Spectra), including Figures S1-S48 and Table S1-S3.

Notes

The authors declare no competing financial interest.

Fluorescent supramolecular polymers are of great interest in the areas of supramolecular chemistry and fluorescent materials.¹ Due to the involvement of non-covalent interactions, they possess good structural versatility and stimuli-driven responsiveness towards microenvironment changes, such as pH,² temperature,³ pressure⁴, and light illumination.⁵ In addition, they inherit the emission characteristics originating from the chromophores incorporated into the polymer, resulting in widespread applications as self-healing materials,⁶ chemical sensors⁷, light-emitting materials,⁸ etc. Generally, the properties of fluorescent supramolecular polymers are dependent on the fluorophore installed on the building blocks and the nature of the non-covalent interactions which tailor the connection of those building blocks. The preparation of fluorescent supramolecular polymers with desired properties is challenging due to the potential incompatibilities and interferences by the incorporation of fluorophores with the self-assembly process.

Over the last decades, investigation in discrete supramolecular coordination complexes (SCCs) has gained attention due to their well-defined sizes and shapes,⁹ and diverse functionalities (photophysical, biological, and catalytic properties).¹⁰ SCCs can exhibit superior properties comparing to the independent building blocks due to the interactions between the building blocks and the unique cyclic topologies, affording a simple and efficient methodology for the bottom-up preparation of functional material at the molecular level. Therefore, supramolecular polymers with novel topological structures as well as photophysical properties can be prepared by the incorporation of SCCs.¹¹ In our previous work, Pt(II) rhomboidal metallacycles with 21-crown-7 moieties and different emission colors were synthesized.¹² Cross-linking the metallacycles by the addition of bis-ammonium salts furnishes fluorescent supramolecular polymers, which emission can be tuned by varying the concentration of the light-emitting building blocks.

Herein, in further pursuit of metallacycle-cored fluorescent supramolecular polymers that possess targeted optical properties, we designed and synthesized a suite of metallacycles **3a-3h** comprised of phenanthrene-21-crown-7 (P21C7)-based 60° diplatinum (II) acceptors and 120° dipyridyl donors. Fluorescence emission spanning the visible region ($\lambda_{\text{max}} = 427\text{--}593\text{ nm}$) was achieved by functional group modifications on the donor. Fluorescent supramolecular polymers were prepared using P21C7-based host-guest interaction, which display similar emission bands, but higher quantum yields relative to their discrete counterparts in both solution and thin film. A white-light emitting LED was fabricated by

placing a yellow-emitting supramolecular polymer **SP-3h** on a UV-emitting LED, indicating the potential of the supramolecular polymers for applications as photo-electronic materials.

As shown in Scheme 1, coordination-driven self-assembly of 120° dipyridyl donors **1a-1h** with phenanthrene-21-crown-7 (P21C7)-based 60° diplatinum (II) acceptor **2** results in the formation of metallacycles **3a-3h** in high yield (>90%) (Figure S1- S42). The resulting metallacycles were characterized by multinuclear NMR and electrospray ionization-time of flight-mass spectrometry (ESI-TOF-MS). Downfield shifts for the pyridyl protons are observed for the metallacycles relative to the free donors, suggesting loss of electron densities upon the formation of platinum-N coordination interaction (Figure S43) in the ^1H NMR. For example, comparing the ^1H NMR spectra of **1c** and **3c** reveal that the α -pyridyl proton H_α (8.62 ppm) splits into H_α' and H_α'' (8.88 and 8.64 ppm), and the β -pyridyl proton H_β (7.61 ppm) splits into H_β' and H_β'' (8.10 and 7.73 ppm) (Figure 1a) for **3c**. The correlation of α , β -pyridyl protons of **3c** was indicated by ^1H - ^1H homonuclear correlation spectroscopy NMR (COSY) experiments (Figure S44). In the ^{31}P NMR, a sharp singlet with concomitant ^{195}Pt satellites is observed for each of the metallacycles (Figure 1c), indicating a single phosphorous environment due to the highly symmetric topologies of the metallacycles. The formation of the metallacycles was further confirmed by ESI-TOF-MS. For example, isotopically resolved peaks correspond to intact entities with charge states arising from the loss of the triflate counterions $[\text{M-3OTf}]^{3+}$ with $m/z = 1124.65$ for **3c** (Figure 1d). The experimental results are in good agreement with the calculated values.

The absorption and emission spectra of the metallacycles are shown in Figures S46, and their optical data are summarized in Table S2. Compared with their corresponding donors **1a-1h** (Figure S45, Table S1), all metallacycles **3a-3h** show a redshift in the absorption and emission spectra. By the variation of the substituents installed in the pyridyl ligands, the fluorescent emission for the metallacycles ranges from 427 nm to 593 nm, spanning the visible light region. Additionally, the metallacycles with an endohedral amino group, or substituents (COOCH_3 , CH_3 , 4-methyl benzene) *para* to the aniline group exhibit higher quantum yields in solution and thin film. The favorable photophysical properties of these metallacycles make them ideal for the construction of tunable fluorescent supramolecular polymers in a wide range from blue to red by changing substituents on the dipyridyl donors of the SCC.

Utilizing the guest binding feature of the P21C7 moieties within the metallacycles, cavity-cored supramolecular polymers were prepared by the addition of bis-ammonium salt **6** into the solution of the metallacycles in a 1:1 molar ratio (Scheme 1).

Concentration-dependent ^1H NMR spectroscopy and two-dimensional diffusion-ordered NMR spectroscopy (DOSY) experiments were performed to provide evidence for the polymerization of the metallacycles. With an increase in the concentration of the metallacycles and **6**, the protons of H_1 and H_2 on the P21C7 moiety gradually shift downfield from 4.45 to 4.47 ppm, and 4.04 to 4.06 ppm, respectively (Figure 2a-2c). In contrast, the protons of H_3 and H_4 that correspond to the linker **6** exhibit an upfield shift. All of these chemical shifts provide evidence for the presence of the host-guest interaction between the P21C7 moiety and **6**.¹² Furthermore, all peaks corresponding to the protons on

the metallacycles and **6** become broader as the concentration of the metallacycles and **6** increased from 2 mM to 100 mM, indicating the formation of a supramolecular polymer (Figure S47).^{7c} DOSY NMR experiments were used to estimate the size of the supramolecular polymers (Figure 2d). The measured average diffusion coefficient (D) is $4.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 2 mM. When the concentration is increased to 100 mM, D decreased by nearly ten-fold to $5.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, indicating the formation of polymeric clusters with increasingly larger size. The phenomenon that D decreases with the increasing degree of polymerization is a distinctive feature of supramolecular polymer systems.^{6c}

The metallacycle-cored supramolecular polymers display similar emission spectra and higher quantum yields in solution compared to the corresponding monomers. The emission spectra of the supramolecular polymers **SP-3c** (constructed from **3c** and **6**) and **SP-3h** (constructed from **3h** and **6**) are shown in Figure 3. The solution of **3c** ($c = 40 \text{ mM}$) displays an emission band centered at 515 nm ($\Phi_{3c} = 0.15$) (Figure 3a), while the emission band red-shifts to 530 nm and the quantum yield increases to 0.18 for **SP-3c** at the same concentration. A similar phenomenon was found in the emission profiles of **3h** and **SP-3h**, exhibiting a red-shift of 15 nm (from 555 nm to 570 nm) and an enhancement of 0.02 ($\Phi_{\text{sp-3h}}=26$) in the quantum yield (Figure 3c).

The emission of the supramolecular polymer thin film, on the other hand, exhibits a blue-shift of 10 nm compared to that in solution (Figures 3b, 3d and Table S3). The quantum yields of the supramolecular polymer thin films are almost double relative to that of their monomer metallacycles ($\Phi_{\text{SP-3c-film}}: \Phi_{3c\text{-film}} = 13: 6$, $\Phi_{\text{SP-3h-film}}: \Phi_{3h\text{-film}} = 22: 15$). To explore the reason for the increase in the quantum yields of the metallacycle-cored supramolecular polymer thin films, scanning electron microscopy (SEM) was employed to investigate the microstructure of metallacycle **3c**, **3h** and their supramolecular polymers **SP-3c** and **SP-3h**. The formation of polymeric structure is known for enhancing the fluorescence efficiency of luminophores in the solid state by reducing the self-quenching and aggregation.¹³ As shown in Figure S48, a structure with tight stacking can be seen in **3c** and **3h**, while the arrangement of **SP-3c** and **SP-3h** appears less dense and more orderly, indicating that the tightly packed structure of the SCCs in the solid state may facilitate the excited state interactions (e. g. formation of non-emissive excimers) that results in loss of excitation energy and a sharp decrease in quantum yield.¹⁴ When a linear dynamic polymer is used to modulate the packing of the SCCs, the tight stacking is weakened, and hence the quenching is reduced, resulting in an enhancement of emission efficiency.

Because of good solubility as well as a high quantum yield, **SP-3h** was utilized as a coating material to extend the emission range of a narrow band light emitting diode (LED) and thereby convert it to a broadband light source. Commercially available UV-LED was used as a photon source and was converted to a white-light source by dipping it in the solution of **SP-3h**. As shown in Figure 4, the original UV-LED displays an emission band centered at 430 nm (CIE chromaticity coordinate: 0.16, 0.05), while the **SP-3h** thin film emission is centered at 560 nm (CIE chromaticity coordinate: 0.38, 0.52). After painting SP-3h on the UV-LED, two bands centered at 430 and 550 nm were observed, extending the emission color from blue to white (Figure 4c-4f). The emission spectra were converted into the CIE

chromaticity diagram. The painted LED was found located at (0.29, 0.34), which belongs to the white-light zone (Figure 4b).

In conclusion, fluorescent supramolecular polymers were constructed by linking P21C7-containing metallacycles using bis-ammonium salt in a 1:1 molar ratio, forming dynamic bonds via host-guest interactions. The supramolecular polymers inherit the tunable fluorescence of the metallacycles by modification on the precursor. Higher emission efficiency is observed upon polymerization in both solution and thin film. SEM studies on the microstructures indicate that the improvement in the quantum yields for the supramolecular polymers is likely the result of alternative stacking patterns of the metallacycles that reduced the loss of the excitation energy. **SP-3h** was used to coat a blue-light LED source, which converted it into a white-light lamp, showing the potential of the supramolecular polymers for the fabrication of light-emitting materials. This study provides a strategy for the fabrication of fluorescent supramolecular polymers with facile tunability by functional group modifications on the precursors, and lays a foundation for the development of self-assembled polymeric materials for photoelectric, bio-imaging and biosensing applications.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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REFERENCES

- (a) Yang L; Tan X; Wang Z; Zhang X Supramolecular Polymers: Historical Development, Preparation, Characterization, and Functions. *Chem. Rev.* 2015, 115, 7196–7239; [PubMed: 25768045] (b) Wei P; Yan X; Huang F Supramolecular Polymers Constructed by Orthogonal Self-assembly Based on Host-Guest and Metal-Ligand Interactions. *Chem. Soc. Rev.* 2015, 44, 815–832; [PubMed: 25423355] (c) Wang H; Ji X; Li Z; Huang F Fluorescent Supramolecular Polymeric Materials. *Adv. Mater.* 2017, 29, 1606117; (d) Abbel R; Grenier C; Pouderoijen MJ; Stouwdam JW; Leclerc PELG; Sijbesma RP; Meijer EW; Schenning APH White-Light Emitting Hydrogen-Bonded Supramolecular Copolymers Based on π -Conjugated Oligomers. *J. Am. Chem. Soc.* 2009, 131, 833–843. [PubMed: 19093865]
- (a) Cafferty BJ; Avirah RR; Schuster GB; Hud NV Ultra-sensitive pH Control of Supramolecular Polymers and Hydrogels: pK_a Matching of Biomimetic Monomers. *Chem. Sci.* 2014, 5, 4681–4686; (b) Ji X; Chen J; Chi X; Huang F pH-Responsive Supramolecular Control of Polymer Thermoresponsive Behavior by Pillararene-Based Host-Guest Interactions. *ACS Macro. Lett.* 2014, 3, 110–113; (c) Zhang S; Bellinger AM; Gletting DL; Barman R; Lee YA; Zhu J; Cleveland C; Montgomery VA; Gu L; Nash LD; Maitland DJ; Langer R; Traverso G A pH-Responsive Supramolecular Polymer Gel as An Enteric Elastomer for Use in Gastric Devices. *Nat. Mater.* 2015, 14, 1065–1071; [PubMed: 26213897] (d) Yao C; Zhang J; Cheng M; Sun Q; Pan Y; Jiang J; Wang L A Four-Armed Unsymmetrical Cryptand: From Two Different Host-Guest Interactions to Responsive Supramolecular Polymer. *Macromol. Rapid Commun.* 2018, 39, 1700218.
- (a) Kumpfer JR; Rowan SJ Thermo-, Photo-, and Chemo-Responsive Shape-Memory Properties from Photo-Cross-Linked Metallo-Supramolecular Polymers. *J. Am. Chem. Soc.* 2011, 133, 12866–12874; [PubMed: 21790172] (b) Schmidt BVKJ; Hetzer M; Ritter H; Barner-Kowollik C UV Light

and Temperature Responsive Supramolecular ABA Triblock Copolymers via Reversible Cyclodextrin Complexation. *Macromolecules* 2013, 46, 1054–1065;(c)Tu Y; Peng F; Sui X; Men Y; White PB; van Hest JCM; Wilson DA Self-Propelled Supramolecular Nanomotors with Temperature-Responsive Speed Regulation. *Nat. Chem.* 2017, 9, 480–486. [PubMed: 28430193]

4. (a) Balkenende DW; Monnier CA; Fiore GL; Weder C Optically Responsive Supramolecular Polymer Glasse. *Nat. Commun.* 2016, 7, 10995; [PubMed: 26983805] (b)Lavrenova A; Balkenende DW; Sagara Y; Schrettl S; Simon YC; Weder C Mechano- and Thermoresponsive Photoluminescent Supramolecular Polymer. *J. Am. Chem. Soc.* 2017, 139, 4302–4305. [PubMed: 28293946]
5. (a) Priimagi A; Cavallo G; Forni A; Gorynsztejn- Leben M; Kaivola M; Metrangolo P; Milani R; Shishido A; Pilati T; Resnati G; Terraneo G Halogen Bonding versus Hydrogen Bonding in Driving Self-Assembly and Performance of Light-Responsive Supramolecular Polymers. *Adv. Funct. Mater.* 2012, 22, 2572–2579;(b)Xu J; Chen Y; Wu L; Tung C; Yang Q Dynamic Covalent Bond Based on Reversible Photo [4 + 4] Cycloaddition of Anthracene for Construction of Double-Dynamic Polymers. *Org. Lett.* 2013, 15 6148–6151; [PubMed: 24237380] (c)Concellon A; Blasco E; Martinez-Felipe A; Martinez JC; Sics I; Ezquerro TA; Nogales A; Pinol M; Oriol L Light-Responsive Self-Assembled Materials by Supramolecular Post-Functionalization via Hydrogen Bonding of Amphiphilic Block Copolymers. *Macromolecules* 2016, 49, 7825–7836;(d)Zhan T; Lin M; Wei J; Liu L; Yun M; Wu L; Zheng S; Yin H; Kong L; Zhang K Visible-light Responsive Hydrogen-bonded Supramolecular Polymers Based on Ortho-Tetrafluorinated Azobenzene. *Polym. Chem.* 2017, 8, 7384–7389.
6. (a) Cordier P; Tournilhac F; Soulie-Ziakovic C; Leibler L Self-Healing and Thermoreversible Rubber from Supramolecular Assembly. *Nature* 2008, 451, 977–980; [PubMed: 18288191] (b)Chen H; Ma X; Wu S; Tian H A Rapidly Self-Healing Supramolecular Polymer Hydrogel with Photostimulated Room-Temperature Phosphorescence Responsiveness. *Angew. Chem. Int. Ed. Engl.* 2014, 53, 14149–14152; [PubMed: 25323299] (c)Zhan J; Zhang M; Zhou M; Liu B; Chen D; Liu Y; Chen Q; Qiu H; Yin S A Multiple-Responsive Self-Healing Supramolecular Polymer Gel Network Based on Multiple Orthogonal Interactions. *Macromol. Rapid. Commun.* 2014, 35, 1424–1429; [PubMed: 24943122] (d)Lu C; Zhang M; Tang D; Yan X; Zhang Z; Zhou Z; Song B; Wang H; Li X; Yin S; Sepehrpour H; Stang PJ Fluorescent Metallacage-Core Supramolecular Polymer Gel Formed by Orthogonal Metal Coordination and Host-Guest Interactions. *J. Am. Chem. Soc.* 2018, 140, 7674–7680. [PubMed: 29856215]
7. (a) Ji X; Yao Y; Li J; Yan X; Huang F A Supramolecular Cross-Linked Conjugated Polymer Network for Multiple Fluorescent Sensing. *J. Am. Chem. Soc.* 2013, 135, 74–77; [PubMed: 23259828] (b)Chen D; Zhan J; Zhang M; Zhang J; Tao J; Tang D; Shen A; Qiu H; Yin S A Fluorescent Supramolecular Polymer with Aggregation Induced Emission (AIE) Properties formed by Crown Ether-Based Host-Guest Interactions. *Polym. Chem.* 2015, 6, 25–29;(c)Xu L; Chen D; Zhang Q; He T; Lu C; Shen X; Tang D; Qiu H; Zhang M; Yin S A Fluorescent Cross-Linked Supramolecular Network formed by Orthogonal Metal-Coordination and Host-Guest Interactions for Multiple Ratiometric Sensing. *Polym. Chem.* 2018, 9, 399–403.
8. (a) Liang A-H; Zhang K; Zhang J; Huang F; Zhu X-H; Cao Y Supramolecular Phosphorescent Polymer Iridium Complexes for High-Efficiency Organic Light-Emitting Diodes. *Chem. Mater.* 2013, 25, 1013–1019;(b)Chu YL; Cheng CC; Yen YC; Chang FC A New Supramolecular Hole Injection/Transport Material on Conducting Polymer for Application in Light-Emitting Diodes. *Adv. Mater.* 2012, 24, 1894–1898. [PubMed: 22415883]
9. (a) Chakrabarty R; Mukherjee PS; Stang PJ Supramolecular Coordination: Self-Assembly of Finite Two- and Three-Dimensional Ensembles. *Chem. Rev.* 2011, 111, 6810–6918; [PubMed: 21863792] (b)Cook TR; Stang PJ Recent Developments in the Preparation and Chemistry of Metallacycles and Metallacages via Coordination. *Chem. Rev.* 2015, 115, 7001–7045; [PubMed: 25813093] (c)Smulders MM; Riddell IA; Browne C; Nitschke JR Building on Architectural Principles for Three-Dimensional Metallosupramolecular Construction. *Chem. Soc. Rev.* 2013, 42, 1728–1754; [PubMed: 23032789] (d)Avram L; Cohen Y Diffusion NMR of Molecular Cages and Capsules. *Chem. Soc. Rev.* 2015, 44, 586–602; [PubMed: 25110858] (e)Wang W; Wang Y; Yang H Supramolecular Transformations within Discrete Coordination-Driven Supramolecular Architectures. *Chem. Soc. Rev.* 2016, 45, 2656–2693; [PubMed: 27009833] (f)Gianneschi NC; Masar MS III; Mirkin CA Development of a Coordination Chemistry-Based Approach for Functional Supramolecular Structures. *Acc. Chem. Res.* 2005, 38, 825–837; [PubMed: 16285706]

- (g)Newkome GR; Moorefield CN From 1 $\rightarrow$ 3 Dendritic Designs to Fractal Supramacromolecular Constructs: Understanding the Pathway to the Sierpinski gasket. *Chem. Soc. Rev.* 2015, 44, 3954–3967; [PubMed: 25316287] (h)Clever GH; Punt P Cation-Anion Arrangement Patterns in Self-Assembled Pd₂L₄ and Pd₄L₈ Coordination Cages. *Acc. Chem. Res.* 2017, 50, 2233–2243. [PubMed: 28817257]
10. (a) Feng H-T; Yuan Y-X; Xiong J-B; Zheng Y-S; Tang B-Z Macrocycles and Cages Based on Tetraphenylethylene with Aggregation-Induced Emission Effect. *Chem. Soc. Rev.* 2018, 47, 7452–7476; [PubMed: 30177975] (b)Brown CJ; Toste FD; Bergman RG; Raymond KN Supramolecular Catalysis in Metal- Ligand Cluster Hosts. *Chem. Rev.* 2015, 115, 3012–3035; [PubMed: 25898212] (c) Ward MD; Raithby PR Functional Behaviour from Controlled Self-Assembly: Challenges and Prospects. *Chem. Soc. Rev.* 2013, 42, 1619–1636; [PubMed: 22797247] (d)Ward MD; Hunter CA; Williams NH Coordination Cages Based on Bis(pyrazolylpyridine) Ligands: Structures, Dynamic Behavior, Guest Binding, and Catalysis. *Acc. Chem. Res.* 2018, 51, 2073–2082; [PubMed: 30085644] (e) Kreno LE; Leong K; Farha OK; Allendorf M; Van Duyne RP; Hupp JT Metal-Organic Framework Materials as Chemical Sensors. *Chem. Rev.* 2012, 112, 1105–1125; [PubMed: 22070233] (f)Zhou Z; Liu J; Rees TW; Wang H; Li X; Chao H; Stang PJ Heterometallic Ru-Pt Metallacycle for Two-Photon Photodynamic Therapy. *Proc. Natl. Acad. Sci. U S A.* 2018, 115, 5664–5669. [PubMed: 29760069]
11. (a) Yan X; Li S; Pollock JB; Cook TR; Chen J; Zhang Y; Jia X; Yu Y; Huang F; Stang PJ Supramolecular Polymers with Tunable Topologies via Hierarchical Coordination-Driven Self-Assembly and Hydrogen Bonding Interfaces. *Proc. Natl. Acad. Sci. USA* 2013, 110, 15585–15590; [PubMed: 24019475] (b) Li Z; Zhang Y; Zhang C; Chen L; Wang C; Tan H; Yu Y; Li X; Yang H Cross-Linked Supramolecular Polymer Gels Constructed from Discrete Multi-pillar[5]arene Metallacycles and Their Multiple Stimuli-Responsive Behavior. *J. Am. Chem. Soc.* 2014, 136, 8577–8589; [PubMed: 24571308] (c)Zhou Z; Yan X; Cook TR; Saha ML; Stang PJ Immobilizing Tetraphenylethylene into Fused Metallacycles: Shape Effects on Fluorescence Emission. *J. Am. Chem. Soc.* 2016, 138, 806–809; [PubMed: 26761393] (d)Zheng W; Chen L; Yang G; Sun B; Wang X; Jiang B; Yin G; Zhang L; Li X; Liu M; Chen G; Yang H Construction of Smart Supramolecular Polymeric Hydrogels Cross-linked by Discrete Organoplatinum(II) Metallacycles via Post-Assembly Polymerization. *J. Am. Chem. Soc.* 2016, 138, 4927–4937. [PubMed: 27011050]
12. (a) Zhang M; Yin S; Zhang J; Zhou Z; Saha ML; Lu C; Stang PJ Metallacycle-Cored Supramolecular Assemblies with Tunable Fluorescence Including White-Light Emission. *Proc. Natl. Acad. Sci.* 2017, 114, 3044–3049. [PubMed: 28265080]
13. (a) Luo J; Lei T; Wang L; Ma Y; Cao Y; Wang J; Pei J Highly Fluorescent Rigid Supramolecular Polymeric Nanowires Constructed Through Multiple Hydrogen Bonds *J. Am. Chem. Soc.* 2009, 131, 2076–2077; [PubMed: 19159299] (b) Luo J; Zhou Y; Niu Z-Q; Zhou Q-F; Ma Y; Pei J Three-Dimensional Architectures for Highly Stable Pure Blue Emission *J. Am. Chem. Soc.* 2007, 129, 11314–11315; [PubMed: 17718567] (c) Li B; Fu Q; Han Y; Bo Z Synthesis and Optical Properties of Dendronized Porphyrin Polymers *Macromol. Rapid Commun.* 2006, 27, 1355–1361; (d) Choi C-L; Yen YOF; Sung HH-Y; Siu AW-H; Jayarathne ST; Wong KS; Williams ID Quantifying enhanced photoluminescence in mixed-lanthanide carboxylate polymers: sensitization versus reduction of self-quenching *J. Mater. Chem.*, 2011, 21, 8547–8549.
14. (a) Wise DL, Wnek GE, Trantolo DJ, Cooper TM, Gresser JD Photonic Polymer Systems: Fundamentals: Methods, and Applications. CRC Press: Boca Raton, FL, 1998.(b) Turro NJ Modern Molecular Photochemistry. University Science Books: Mill Article Valley, CA, 1991.(c) Malkin J Photophysical and Photochemical Properties of Aromatic Compounds. CRC Press: Boca Raton, FL, 1992;(d) Birks JB Photophysics of Aromatic Molecules. Wiley: New York, 1970; Vol. 71.

Figure 1. (a) Partial ^1H NMR spectra of **3c** and (b) **1c** (CD_2Cl_2 , 298 K, 500 MHz); (c) $^{31}\text{P}\{^1\text{H}\}$ NMR of **3c**; (d) Experimental (red) and calculated (blue) ESI-TOF-MS spectra of **3c**.

Figure 2. Partial ^1H NMR spectra (CD_3COCD_3 : $\text{CD}_2\text{Cl}_2 = 1:1$ v/v, 298 K, 500 MHz) of **3c** (a), and equal molar **6** and **3c** at the concentration of 100 mM (b), the bisammonium linker **6** (c); (d) measured weight average diffusion coefficient D of equal molar **3c** and **6** at different concentrations.

Figure 3.

Comparison of emission profiles of the supramolecular polymers in the solution (a) **3c** and **SP-3c**, (c) **3h** and **SP-3h** ($c = 40$ mM, $\text{CH}_2\text{Cl}_2 : \text{CH}_3\text{COCH}_3 = 1:1$, v/v); the comparison in emission spectra of the supramolecular polymers in thin film (b) **3c** and **SP-3c**, (d) **3h** and **SP-3h** ($\lambda_{\text{ex}} = 365$ nm).

Figure 4.

(a) Emission spectra of energized painted LED, solution of **SP-3h**, and energized unpainted LED; (b) CIE chromaticity coordinates of the painted LED, solution of **SP-3h**, and energized LED. Photos from unpainted (c-d) and painted (e-f) UV-LEDs under 365 nm illumination: (c) LED off; (d) LED on; (e) lamp coated with **SP-3h** (LED off); (f) lamp coated with **SP-3h** (LED on).

Scheme 1.

Cartoon Representation of the Formation of the Metallacycles (a) and the Fluorescent Supramolecular Polymer from Metallacycles and Bisammonium salt 6 (b).