Supporting Information

Allostery in Molecular Self-Assemblies: Metal Ions Triggered Self-Assembly and Emission of Terthiophene

Shuai Liu, Li Zhao, Yunlong Xiao, Tian Huang, Jianbin Huang*and Yun Yan*

Experimental Section

Materials: TTC4L was synthesized according to the procedure reported in our previous work.[1] Metal nitrates, and other chemicals (A.R. Grade of Beijing Chemical Co.) were used as received.

Sample preparation: The solutions were obtained by dissolving the solid TTC4L powder in the 1:1 water/ethanol (v/v) mixed solvent. The pH of TTC4L solution was about 7.3. The pH values of TTC4L solutions were measured using a SevenMulti type pH meter with InLab Semi-Micro electrodes (Mettler Toledo, Switzerland). The organic-inorganic hybrid microspheres can be obtained by directly vortex mixing TTC4L solution with desired amount of concentrated metal nitrate solution. In a typical procedure, 2 mL of 0.50 mM TTC4L and 200 μL 50 mM silver nitrate were mixed at the molar ratio of 1:1 and the resulting mixture was then equilibrated at 25 °C for one day before further analysis. During this period, some yellow precipitates can be observed at the bottom of the test tubes, which were collected 24 hours' later by centrifugation and washed with deionized water for several times.

Characterization: The self-assembled structures of TTC4L-M^{n+} assemblies were characterized by scanning electron microscopy (SEM, Hitachi S4800, 10 kV), A1R-si inverted confocal laser scanning microscope (CLSM, Nikon, Japan), respectively. Fluorescence measurements were carried out on the Edinburgh F7000 fluorescence spectrophotometer. X-ray diffraction (XRD, Rigaku Dmax-2000, Ni-filtered Cu Kα radiation), environmental scanning electron microscope (ESEM, Quanta 200FEG,15kV) together with energy-dispersive spectroscopy (EDS) measurement. All measurements were conducted under ambient conditions at room temperature.

For SEM measurements, the samples were dropped onto a silicon wafer, and a copper grid respectively, followed by drying in ambient air at room temperature.For CLSM measurements, one drop of the sample was placed onto a clean glass slide, which is sealed with a covering glass. For XRD measurements, solid samples were put on clean glass slide.

Theoretical calculations

The coordinating modes and the corresponding energies were calculated at restricted density functional theory level. The hybrid functional B3LYP and the 6-311+g(d,p) basis set were used. All calculations were performed using the Gaussian09 package.

Elemental analysis (EDS) of TTC4L-Ag^+ assemblies

Table S1 X-ray energy dispersive spectroscopy results of TTC4L- Ag^+ assemblies.

System	C	S	O	Ag	S/Ag	TTC4L/Ag^+
TTC4L-Ag^+	73.1-73.2	7.1-8.3	12.0-13.2	2.4-2.8	3	1:1

Low angle X-ray diffraction of TTC4L-Ag^+ systems

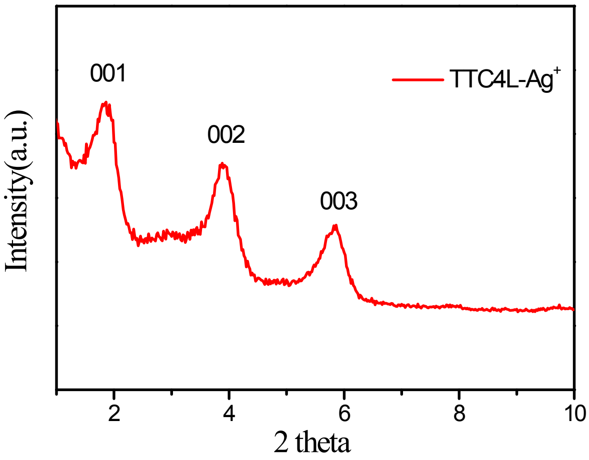


Fig. S1 XRD patterns of TTC4L-Ag$^+$ microspheres at low angel region.

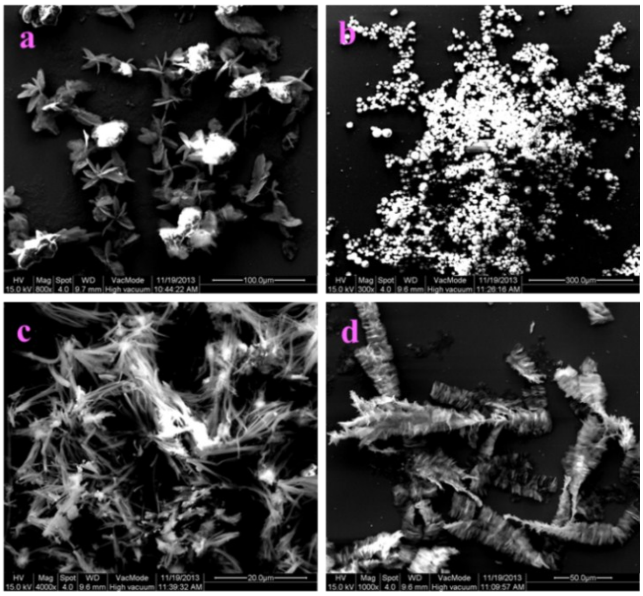
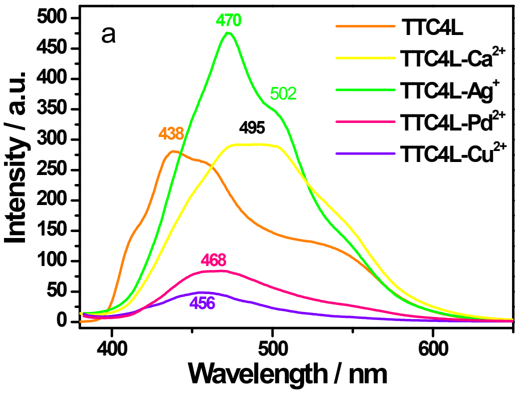


Figure S2. ESEM images of the TTC4L-metal ionsassemblies (a) TTC4L-Ca^{2+}, (b) TTC4L-Ag$^+$, (c) TTC4L-Pd^{2+} and (d) TTC4L-Cu^{2+}.

Fluorescence emission colors of TTC4L-Metal ion systems



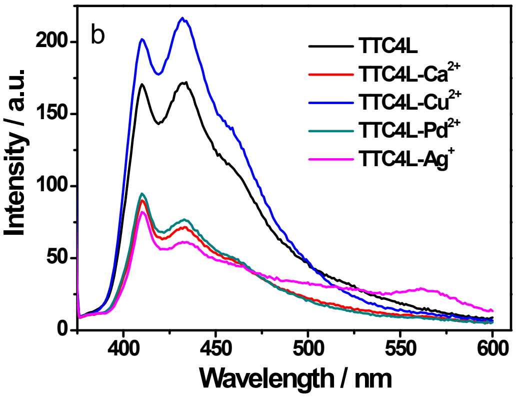


Figure S3. Solid FL emission spectra for the TTC4L-metal ions assemblies (a) and the emission of molecularly dissolved TTC4L-metal ions coordinating complexes in ethanol (b). (λ_{ex} = 365 nm)

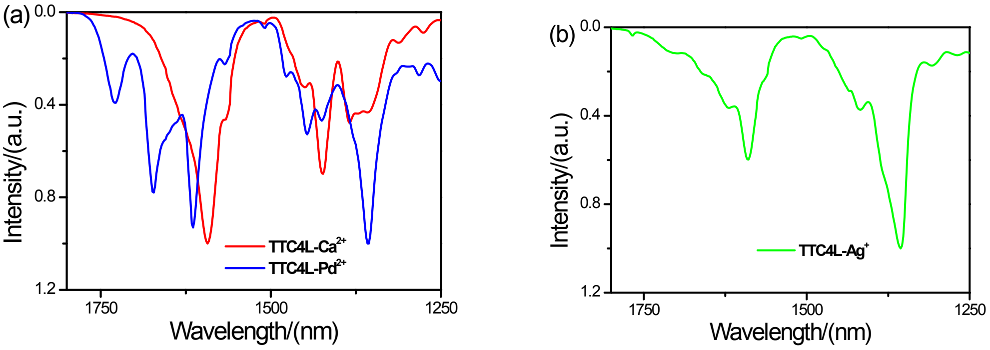
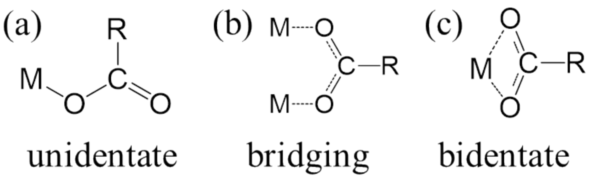


Figure S4. FT-IR spectra of TTC4L-metal ionsassemblies (a) TTC4L-Ca^{2+} and TTC4L-Pd^{2+}, (b) TTC4L-Ag^{+} and TTC4L-Cu^{2+}.

FT-IR spectroscopy was used to diagnose the coordination mode of the carboxylate ligands. It is well-known in literature that the wave number separation between the asymmetric and symmetric stretching vibration of COO^{-} groups corresponds to different coordinating states. $\Delta\nu_{as}$>>200 cm^{-1} suggesting unidentate binding, as illustrated in Scheme S1a; $\Delta\nu_{as} \approx 200$ cm^{-1} for bridging binding (Scheme S1b); and $\Delta\nu_{as}$<< 200 cm^{-1} bidentate binding (Scheme S1c).[2-4] The strong characteristic bands of carboxyl groups for the asymmetric and for the symmetric vibrations are analyzed as shown in Table S2. From the separations ($\Delta\nu_{as}$), the coordination mode of the carboxylate ligands can be ascribed that Ag^{+} and $Pd^{2+}$are coordinate with carboxyl in unidentate fashion, and Ca^{2+}, Cu^{2+} in bridging or unidentate fashion.



Scheme S1 The coordination mode of the carboxylate ligands with metal ions.

Table S2 FT-IR results of TTC4L-metal ion systems.

	TTC4L-Ca^{2+}	TTC4L-Pd^{2+}	TTC4L-Ag^{+}
ν_s/cm^{-1}	1357/1384	1357	1355
ν_{as}/cm^{-1}	1593	1673	1590
$\Delta\nu$/cm^{-1}	209/236	316	235
Modes	unidentate bridging	unidentate	unidentate

Supplementary Reference

1. L. Zhao, X. H. Cheng, Y. Ding, Y. Yan and J. B. Huang, *Soft Matter*, 2012, **8**, 10472-10478.
2. H. L. Gao, B. Ding, L. Yi, P. Cheng, D. Z. Liao, S. P. Yan and Z. H. Jiang, *Inorganic Chemistry Communications*, 2005, **8**, 151-154.
3. G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev.*, 1980, **33**, 227-250.
4. Y. Lan, L. Xu, Y. Yan, J. Huang, A. de Keizer, N. A. M. Besseling and M. A. C. Stuart, *Soft Matter*, 2011, **7**, 3565-3570.