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Solvent-Dependent Supramolecular Host–Guest Assemblies of Platinum(II) Tweezers and a Guest System: From Discrete Molecules to High-Ordered Aggregates

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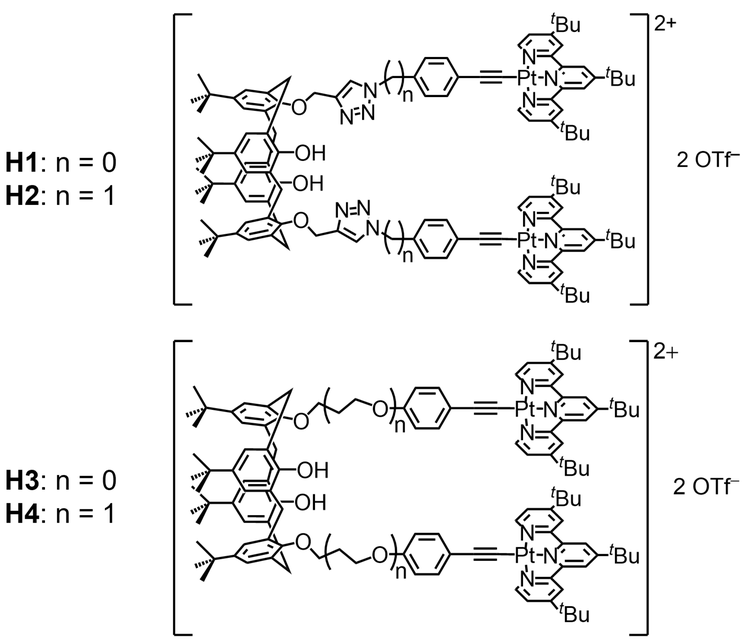
Introduction

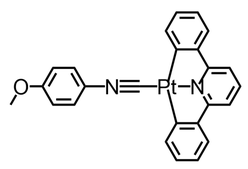
A series of platinum(II) calix[4]arene-based molecular tweezers was synthesized. The studies of the host–guest association with a charge-neutral cyclometalated platinum(II) complex showed a drastic color change and the turning on of near-infrared emission resulting from Pt···Pt and π–π interactions. Control of the host–guest assembly process by varying the solvent composition can lead to a change from discrete host and guest molecules to high-ordered host–guest oligomers with the formation of sheet-like nanostructures, demonstrating a rare example of three-state supramolecular host–guest system with high solubility in solvents of diverse polarity. The change in host–guest assembly behaviors could be probed by drastic color changes from yellow to orange to green. The present study provides insights into the systematic design of solvent-responsive molecular materials using molecular tweezers-directed host–guest assembly, with potential applications in colorimetric sensing of changes in the micro-environment.

Chemical Structures

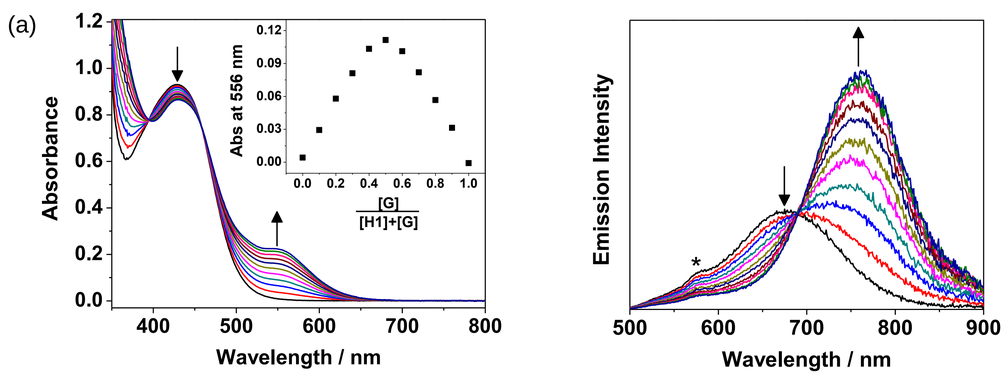
Calix[4]arene-based Host complexes

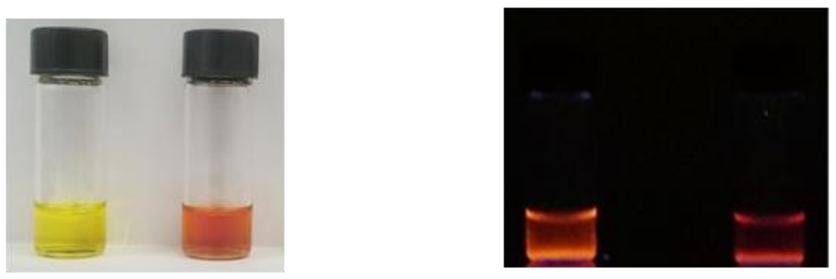


Guest complex

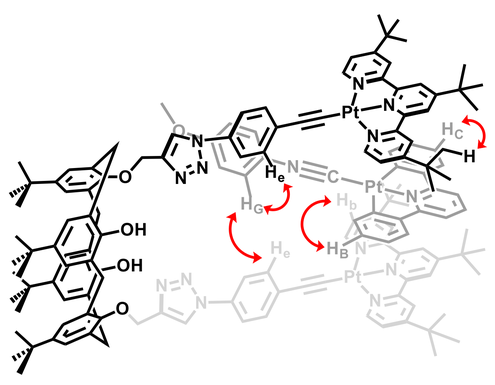


Host–Guest Binding Studies





(c)



(a) (Left) UV-Vis absorption and (Right) emission spectral changes on addition of **G** into (a) **H1** ($[\mathbf{H1}]_o = 8 \times 10^{-5}$ M) (the asterisk denoted an instrumental artifact); (b) (Left) Color and (Right) emission changes of **H1** upon addition of one equivalent of **G** in acetonitrile (1.6×10^{-4} M). (From left to right, **H1** only, and [**H1**·**G**]); (c) The plausible association mode of **H1** and **G** (arrows indicate interaction that results in the cross peaks in ^{1}H–^{1}H ROESY NMR spectra of **H1** with one equivalent of **G** in CD_3CN at 298 K)

Contact information

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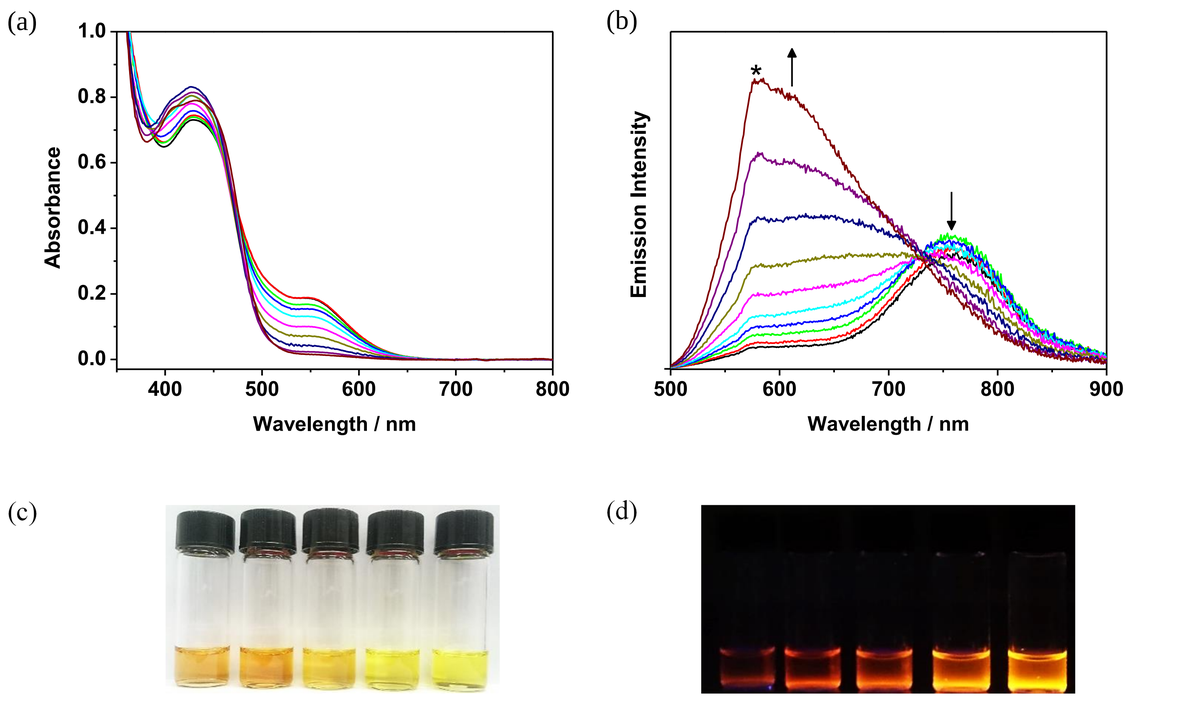
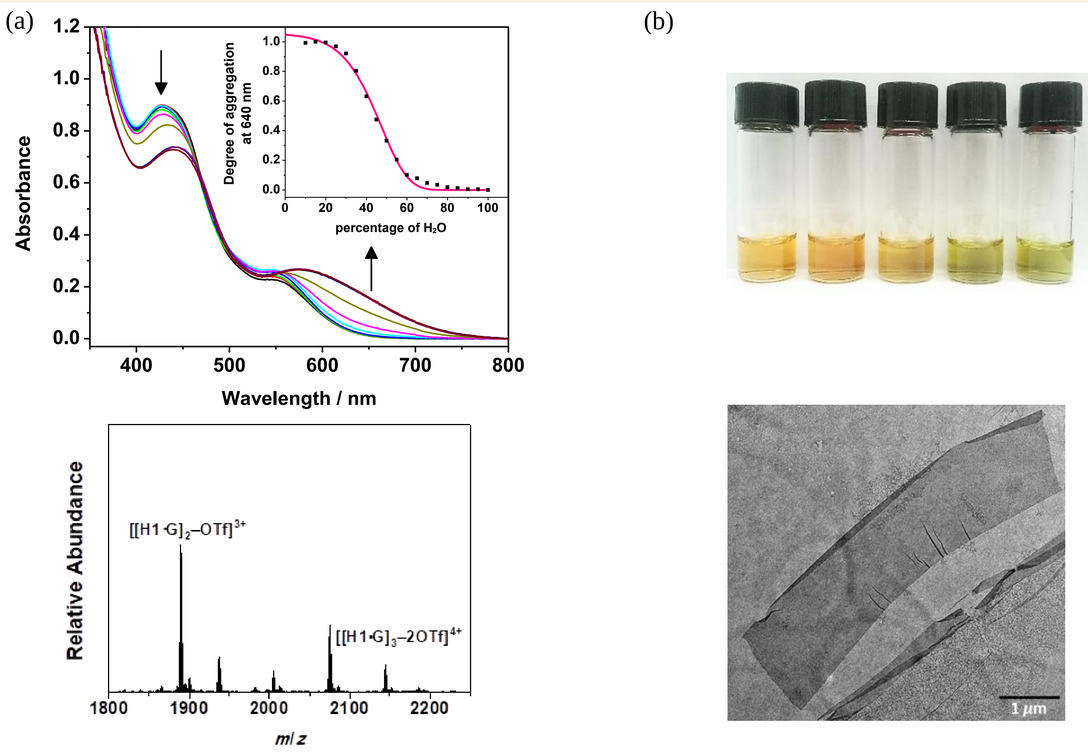
Solvent-Induced Host–Guest Adduct Disassembly in Acetonitrile–Dichloromethane Mixture



(a) UV-Vis absorption and (b) emission spectral changes of [**H1**·**G**] adduct in acetonitrile ([**H1**·**G**] = 8×10^{-5} M) upon increasing dichloromethane content (the asterisk denoted an instrumental artifact); (c), (d) solutions of [**H1**·**G**] adduct in acetonitrile–dichloromethane mixture (percentage of dichloromethane in acetonitrile from left to right: 0, 30, 50, 70, 90 %)

Solvent-Induced Host–Guest Adduct Aggregation in Acetonitrile–Water Mixture



(a) UV-Vis absorption spectral changes of [**H1**·**G**] adduct in acetonitrile ([**H1**·**G**] = 8×10^{-5} M) upon increasing water content (the asterisk denoted an instrumental artifact); (b) solutions of [**H1**·**G**] adduct in acetonitrile–water mixture (percentage of water in acetonitrile from left to right: 0, 40, 50, 70, 90 %) Inset shows a plot of normalized degree of aggregation against volume fraction of water; (c) High-resolution positive ESI-mass spectrum of [**H1**·**G**] in CH_3CN–water (3:7 v/v); (d) TEM image of [**H1**·**G**] adduct in CH_3CN–water (3:7 v/v)

Conclusion

- A series of calix[4]arene-based alkynylplatinum(II) terpyridine molecular tweezers has been successfully designed and synthesized, demonstrating multi-addressable host–guest assembly behavior with a charge-neutral cyclometalated platinum(II) guest.
- Upon the variation in solvent polarity, this class of tweezers complexes exhibited distinct host–guest assembly properties from dynamic reversible host–guest interaction to high-ordered inter-adduct assembly, demonstrating a bottom-up strategy in constructing molecular architectures using directional non-covalent Pt···Pt interactions.
- The present study can provide further insights into the systematic design of multi-addressable molecular systems through the precise manipulation of Pt···Pt interactions in the tweezers-directed host–guest assembly in response to the solvent environment.

Acknowledgement

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Reference

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