Tetrahedron 74 (2018) 2792–2796

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Supramolecular polymers from coronene multicarboxylates and multipyridiniums in water stabilized by ion-pair attraction and aromatic stacking

Qi Qi, Bo Yang, Hui Wang, Dan-Wei Zhang[**], Zhan-Ting Li[*]

Department of Chemistry, Collaborative Innovation Centre of Chemistry for Energy Materials (iChEM), Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, 2205 Songhu Road, Shanghai 200438, China

A R T I C L E I N F O

Article history:
Received 17 March 2018
Received in revised form
12 April 2018
Accepted 17 April 2018
Available online 18 April 2018

Keywords:
Supramolecular polymers
Electrostatic attraction
Aromatic stacking
Aqueous phase
Multivalence

A B S T R A C T

Coronene tatracarboxylate **CTC** and octacarboxylate **COC** have been utilized to interact with dipyridinium **DP** and tetrapyridinium **TP** to assemble new supramolecular polymers in water. It was revealed that **CTC** interacted with **DP** and **TP** in 1:2 and 1:1 stoichiometry, whereas the binding between **COC** and **DP** and **TP** occurred in 1:4 and 1:2 stoichiometry. For all complexations, **DP** and **TP** behaved as a uni- or siamesed tweezers to clamp **CTC** or **COC** driven by ion-pair attraction and hydrophobically driven stacking of the pyridinium and coronene units. Apparent association constants were determined to be 33400 (**CTC/DP**), 9400 (**COC/DP**), 151000 (**CTC/TP**), and 89000 (**COC/TP**) M^{-1}, respectively, for the single clamping binding motif of the four complexes. Dynamic light scattering and isothermal titration calorimetric experiments supported that the mixtures of **CTC** and **COC** with **TP** formed linear and cross-linked supramolecular polymers.

1. Introduction

Supramolecular polymers emerged from the combination of covalently bonded polymers and supramolecular binding motifs.[1–7] Pioneering works by Lehn and Meijer triggered extensive applications of hydrogen bonding as driving force for the formation of supramolecular polymers.[8–14] Currently other noncovalent forces,[15–25] including coordination, donor-acceptor interaction, and solvophobicity, have also found wide applications. In most cases, the self-assembly is realized in organic solvents of low polarity. More recently the construction of such kind of self-assembled architectures in aqueous media has received increased interest due to their more promising potential in the development of biocompatible materials.[26–28] In this context, hydrophobicity-driven encapsulation of cyclodextrins and cucurbiturils for hydrophobic monomeric or dimeric species has been vigorously investigated as connecting motifs.[29–32] A more straightforward choice might be to directly make use of ion-pair electrostatic attraction for stabilizing this family of advanced architectures to acquire good water-solubility and biocompatibility. However, single ion-pair interaction does not allow efficient binding due to the competitiveness of water. A successful approach reported by Schmuck and co-workers has involved the combination of ion-pair electrostatic attraction and multiple hydrogen bonds through the principle of multivalency,[33,34] which has led to the generation of switchable supramolecular systems in polar solvents.[35,36]

Centrosymmetric multitopic monomers have been designed for building a number of three-dimensional (3D) cross-linking supramolecular networks through multivalency effect,[37] with hydrogen bonding,[38] hydrophobicity,[39,40] radical cation stacking as driving force.[41–44] Previously we reported that multivalent ion-pair binding, assisted by aromatic stacking, could realize extremely high stability of the resulting complexes in water.[45,46] Herein we describe that strong binding between coronene tetra- and octacarboxylates (**CTC** and **COC**) and tetrapyridinium derivative (**TP**) (Fig. 1), which was driven by multiple ion-pair electrostatic attractions and aromatic stacking, could lead to the formation of linear and cross-linking supramolecular polymers in water.

---

[*] Corresponding author.

[**] Corresponding author.

E-mail addresses: zhangdw@fudan.edu.cn (D.-W. Zhang), ztli@fudan.edu.cn (Z.-T. Li).

https://doi.org/10.1016/j.tet.2018.04.047

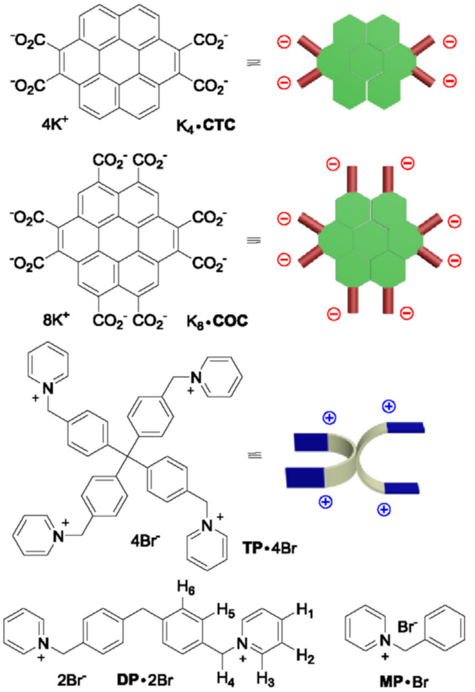

Fig. 1. The structure of K_4•**CTC**, K_8•**COC**, **TP**•4Br, **DP**•2Br and **MP**•Br and schematic representation of the first compounds.

2. Results and discussion

Highly water-soluble coronene multicarboxylates **CTC** and **COC**, both as K^+ salt, were chosen as aromatic multianions for studying ion-pair interaction in water. Tetrapyridinium **TP**, as Br^- salt and also highly soluble in water, was designed as cationic counterpart, which was expected to function as siamesed tweezers to clamp the two coronene derivatives through ion-pair attraction and possible stacking between the pyridinium and coronene units.[47–50] For comparison, **DP** and **MP**, both as Br^- salt, were also prepared.

The interactions of **CTC** and **COC** with control **DP** were first investigated by ^1H NMR in D_2O. At high concentrations, aggregation caused the signals of **CTC** to decrease considerably (Fig. 2a). Adding **DP** caused these signals to shift upfield significantly and this shifting reached the maximum when 2.0 equivalent of **DP** was added ($\Delta\delta = -0.21$ ppm). Further addition of another 2.0 equivalent of **DP** only caused 0.02 ppm of upfield shifting. Notably, in the presence of 2.0 equivalent of **DP**, the signals of **CTC** turned back to two doublets of higher resolution. This result supported that **DP** suppressed its important intermolecular stacking, which might be attributed to a 2:1 clamping binding in which two **DP** tweezers held one **CTC** molecule, with the pyridinium units of **DP** stacking with its coronene unit from the two sides. This 2:1 binding pattern was also consistent with the above ^1H NMR observation that 2.0 equivalent of **DP** caused maximum upfield shifting of the signals of **CTC**. Adding **DP** (1.0 equiv) caused no observable shifting ($\Delta\delta < 0.01$ ppm) for the singlet of **COC** in the ^1H NMR spectrum (Figs. S1 and S2). Thus, ^1H NMR spectra were further recorded for **DP** with the addition of **COC** in D_2O (Fig. 2b). It was found that 0.25 equivalent of **COC** caused maximum upfield shifting for the H-1-6 signals of **DP** in the downfield area, with $\Delta\delta = -0.45$, -0.47, -0.51, -0.60, -0.56, and -0.60 ppm, respectively. Further adding **COC** (1.0 equiv) led to very small shifting (-0.02~-0.05 ppm). These observations supported a 4:1 binding pattern. The fact that the ^1H NMR signal of **COC** did not shift upon mixing with **DP** suggested a binding motif that was different from that formed between **CTC** and **DP**.

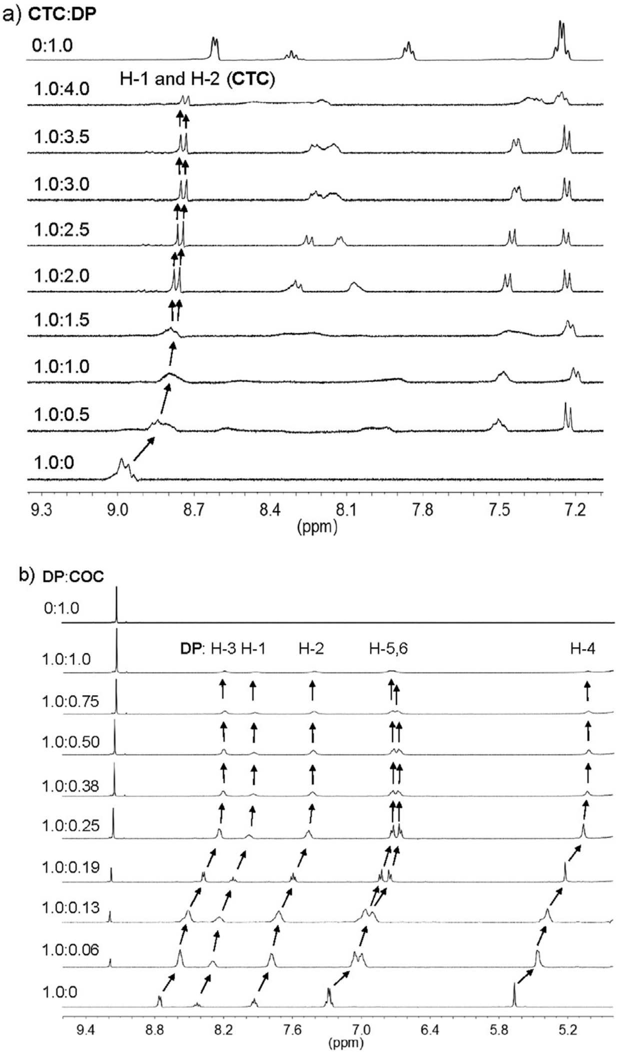

Fig. 2. Partial ^1H NMR (400 MHz) spectra of the mixtures of a) **CTC** (2.0 mM) and **DP** (0–8 mM) and b) **DP** (4.0 mM) and **COC** (0–4 mM) in D_2O at 25 °C.

For the mixture of **CTC** and **DP**, the **DP** tweezers should clamp the coronene ring of **CTC** from the two opposite CO_2^--free directions. As a result, the two protons could suffer important shielding of **DP**. For **COC**, the interactions with **DP** might occur from the directions determined by the four neighbouring carboxylate pairs. Through this binding motif, the coronene ring of **COC** could impose shielding on the protons of **DP**, whereas **DP** could not on the coronene protons due to large distance. ^1H NMR spectra of the mixtures of **CTC** and **COC** with **TP** revealed similar shifting behaviour as observed above for their mixtures with **DP** (Figs. S3 and S4), which showed that their binding occurred with a 1:1 and 1:2 stoichiometry. The ^1H NMR experiments for the mixture of **COC** with **DP** and **TP** also excluded the possibility of **DP** or **TP** approaching the coronene ring of **COC** from the directions perpendicular to its two surfaces, which would produce shielding on the coronene protons.

Adding **TP** to the solution of **CTC** or **COC** in water also led to considerable hypochromic effect and bathochromic shifting (3.6 and 3.5 nm, respectively) for their maximum absorbance (Fig. 3). Job's plot for both mixtures revealed a 1:1 and 2:1 binding