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Supporting Information

ABSTRACT: The predesigned metal–organic macrocycle 

\[ \text{Zn}_n \text{QDB}_{13} \text{NO}_3 \] (Zn-QDB) was observed to self-assemble into a hollow, spherical, single-layered “blackberry-type” structure. The self-assembly behaviors of the Zn-QDB are significantly influenced by additional small ions. Specifically, the cations exhibit strong co-ion effects on the interaction between cationic macrocycles which are different from the previously reported co-ion effects of simple anions on anionic polyoxometalates. This unusual phenomenon is due to the unique cation–π interaction between small cations and electron-rich cavity of Zn-QDB, as confirmed by UV–vis, 1H NMR, and fluorescence spectra. The variation of hydrodynamic radius \( R_h \) of assemblies with the changes of solution ionic strength and the type of cations reveals the competition between counterion-mediated attraction and cation–π interaction during the self-assembly process. Furthermore, the cooperativity of cation–π interaction and π–π stacking play a vital role in enhancing the stability of the supramolecular structure.

1. INTRODUCTION

Co-ion effects, interferences from ions with same charges to the measured ion, are ubiquitous in chemistry and biology. In the past century, these effects have been intensely studied and explained by fruitful theories like DLVO theory, Collins’ rules, and Hofmeister effects. Although the co-ion effects have usually been assumed too small or negligible, in some cases the co-ions significantly influenced the physical behaviors of target molecules. For example, in the conformational equilibria of rhodopsin, addition of different co-ions gave different results for the formation of meta 2 rhodopsin. Ninham and co-workers theoretically explained the role of co-ions in this effect by ionic dispersion potentials and ion-specific surface \( \text{pH} \). However, compared with numerous works in protein, electrolyte solutions, and colloid chemistry, the studies of co-ion effects on macroion systems are rarely reported.

Macrons, such as polyoxometalate (POM) anions and metal–organic cationic cages, functionalized with nanoscale sizes between simple ions and colloidal suspensions, exhibit completely different solution behaviors which cannot be described either by Debye–Hückel theory or by DLVO theory. These macrons can self-assemble into higher ordered, hollow, spherical, single-layered “blackberry-type” structures in solution. The self-assembly studies of POM solutions with small amount extra electrolyte show that the co-ions usually play minor roles in the POMs solutions, and there is no obvious influence on the thermodynamic properties of the POMs during self-assembly process. Nonetheless, an intriguing phenomenon was observed recently that the chiral co-ions can selectively suppress the self-assembly process of the enantiomeric POMs to achieve a chiral selection. Therefore, the co-ion effects on the self-assembly of macroions are still not fully explained. Here we report a strong co-ion effect on the solution behaviors of cationic macroions via cation–π interaction.

Cation–π interaction, a binding force between a positive charge and the quadrupole moment of the aromatic systems, has been gradually recognized as one of the strongest among noncovalent interactions and plays an essential role in biological systems, such as stabilizing the peptide structures, protein–ligand interactions as well as ion channels. To reveal the crucial nature of the cation–π interaction, many research groups have devoted efforts to synthesize diverse artificial cation receptor models with electron-rich aromatic cavities. Dougherty and co-workers demonstrated that a variety of synthetic cation receptors could bind positively charged substrates with appreciable affinity via cation–π interaction in both aqueous and organic solvents. Moreover, the cation–π interaction was also confirmed to exist in nanomaterials including nanotubes, nanocapsules, nanospheres with significant effects on their structures and function.

In this work, we use metal–organic macrocycles (MOMs) as cationic macroion models to explore the co-ion effects on their solution behaviors. Metal–organic macrocycles are constructed by coordination bonds between predesigned organic ligands.
2. RESULTS AND DISCUSSION

Molecular Structure of the Metal–Organic Macrocyle Zn-QDB. \( \text{Zn}_3\text{QDB}(\text{NO}_3)_4 \) prepared by the coordination of zinc(II) ions with aromatic-rich ligands QDB (QDB = \(((\text{N}1\text{E},\text{N}3\text{E})\cdot 5\cdot (\text{dibenzyliamino})\cdot \text{N}1\cdot \text{N}3\cdot \text{bis}(\text{quinolin}-2\text{-ylmethylene})\cdot \text{isophthalohydrazide})\)) is chosen as the model macrocation.\(^{15c}\) The single-crystal X-ray structural analysis reveals that Zn-QDB shows a calix[3]arene-like macrocycle structure with \( \sim 2 \) nm in diameter and \( \sim 1 \) nm in height. The structure analysis indicates that the electrons are extensively delocalized over the entire molecular skeleton resulting in an electron-rich cavity. Additionally, the presence of intense \( \pi \) intermolecular \( \pi \) stacking interaction in the crystal structure (Figures 1a and S1).

To eliminate the hydrophobic interaction that dominates affinity in aqueous media, the Zn-QDB crystals are readily dissolved in acetonitrile. The UV–vis spectra, \(^1\)H NMR spectroscopy, as well as ESI-MS spectra of Zn-QDB in CH\(_3\)CN solution confirm that the structure of Zn-QDB is stable (Figures 1b, and S2). Subsequently, the solution conductivities of Zn-QDB with a sequence of concentration are measured (Figure S3). The results show a linear relationship between conductivity and concentration indicating that all the NO\(_3^–\) ions are released and each macrocycle carries 4 positive charges which are attributed to the three Zn\(^{2+}\) ions and the deprotonation of two amide groups in three ligands. The charges distribute in the core of macrocycle, and the arene rings are located on its exterior. Consequently, the property of a special conjugated electron-rich \( \pi \) structure as a cation receptor and the nature of positively charged macrocations in solution make Zn-QDB an ideal model for studying the cationic co-ion effects on the macroion system via cation–\( \pi \) interaction.

Existence of Cation–\( \pi \) Interaction between Additional Cations and Cationic Macrocycles. To confirm the existence of the cation–\( \pi \) interaction in our systems, UV–vis spectra, fluorescent spectra, and NMR titration studies are applied to characterize the sample solutions. In the UV–vis studies (Figure 1b), small amounts of 9 mM NaCl CH\(_3\)CN solutions were continuously titrated into the Zn-QDB CH\(_3\)CN solution (1.0 mL 0.1 mg mL\(^{-1}\)), with molar ratio \( n_{\text{Na}}/n_{\text{Zn-QDB}} = x:1 \) (\( x = 2, 4, 6 \)). The coordinated ligands QDB exhibit absorption bands at 280 and 367 nm, and the peak at 428 nm is attributed to the LMCT absorption of the coordination bond between Zn\(^{2+}\) ions and quinoline groups. Significant incensement of absorbances at 280 and 367 nm was observed with the addition of NaI, while the absorbance at 428 nm kept constant. When \( 6 \) equiv of NaI was added, an obvious red shift from 428 to 446 nm was observed. The results demonstrate that the sodium ions are bonded to the conjugated \( \pi \) orbital of Zn-QDB without affecting the coordination of zinc ions under 6 equiv Na\(^{+}\) ions, suggesting that the cation–\( \pi \) interaction does exist in the Zn-QDB solution. Additionally, the red shift at 428 nm provides an insight in the occurrence of \( \pi \)–\( \pi \) stacking between phenyl rings and quinolinyl rings, since the \( \pi \)–\( \pi \) stacking interaction could be enhanced from subtle to substantial in the presence of cations. Furthermore, the fluorescent intensity of Zn-QDB decreases in the fluorescence titration experiments, and the shifts of protons of QDB ligand in the \(^1\)H NMR studies (Figure 1b), small amounts of 9 mM NaCl CH\(_3\)CN solutions were continuously titrated into the Zn-QDB CH\(_3\)CN solution (1.0 mL 0.1 mg mL\(^{-1}\)), with molar ratio \( n_{\text{Na}}/n_{\text{Zn-QDB}} = x:1 \) (\( x = 2, 4, 6 \)). The coordinated ligands QDB exhibit absorption bands at 280 and 367 nm, and the peak at 428 nm is attributed to the LMCT absorption of the coordination bond between Zn\(^{2+}\) ions and quinoline groups. Significant incensement of absorbances at 280 and 367 nm was observed with the addition of NaI, while the absorbance at 428 nm kept constant. When \( 6 \) equiv of NaI was added, an obvious red shift from 428 to 446 nm was observed. The results demonstrate that the sodium ions are bonded to the conjugated \( \pi \) orbital of Zn-QDB without affecting the coordination of zinc ions under 6 equiv Na\(^{+}\) ions, suggesting that the cation–\( \pi \) interaction does exist in the Zn-QDB solution. Additionally, the red shift at 428 nm provides an insight in the occurrence of \( \pi \)–\( \pi \) stacking between phenyl rings and quinolinyl rings, since the \( \pi \)–\( \pi \) stacking interaction could be enhanced from subtle to substantial in the presence of cations. Furthermore, the fluorescent intensity of Zn-QDB decreases in the fluorescence titration experiments, and the shifts of protons of QDB ligand in the \(^1\)H NMR studies (Figure S4).

Self-Assembly of the Macrocycles into Blackberries. First, the self-assembly behavior of Zn-QDB in CH\(_3\)CN without involving co-ion effect is studied as a starting point. The macrocycle Zn-QDB was dissolved in CH\(_3\)CN at 0.1 mg mL\(^{-1}\) to form a clear solution. Low scattered intensity was collected by means of static light scattering (SLS), suggesting that the macrocycles remain as discrete macrocations in solution and the potential effect of solvent-phobic interaction is excluded. After a long lag period around 60 days, the total scattered intensity started to continuously increase until reaching an equilibrium state after a month at a very high level of \( \sim 5000 \) kcps, indicating the formation of large structures in solution (Figure 1a). The dynamic light scattering (DLS), SLS, atomic force microscopy (AFM), and TEM studies indicate the existence of hollow, spherical, blackberry-type assemblies with hydrodynamic radius (\( R_{h,0} \)) of 42 nm (Figures...
Considering that both MOMs and metal–organic nanocages are macrocations in solution\textsuperscript{16} and both self-assemble into blackberry-type structures, it is reasonable to postulate that their self-assemblies may have a similar major driving force, that is, counterion-mediated attraction. Previously, Würthner has reported that \( \pi-\pi \) stacking has significant impact on the formation of extended assemblies.\textsuperscript{16} To confirm the major driving force of self-assembly is not the \( \pi-\pi \) stacking, the UV–vis spectra of the prepared salt-free Zn-QDB solution was recorded with time. The results showed that the absorption curves remained unchanged during the lag period but continuously decreased with time when the intensity increases, indicating that the Zn-QDB monomers are decreasing and the absorption peak of formed large assemblies becomes lower and broader. However, no significant peak shift was observed with time, indicating the \( \pi-\pi \) stacking scarcely exists or only makes a small contribution to the self-assembly (Figure 2d).

**Co-Ion Effects on the Self-Assembly Behaviors of Macrocycles.** After exploring the solution behaviors of Zn-QDB without the influences from co-ions, additional electrolyte (NaI) was introduced to the Zn-QDB solution to form a more complicated system with co-existence of counterion-mediated attraction, cation–\( \pi \) interaction, as well as the \( \pi-\pi \) stacking. In the self-assembly process of Zn-QDB, there are two hypotheses about the role of co-ions. First, it is assumed that several cations (Na\textsuperscript{+}) are captured by the conjugated \( \pi \) system of one positively charged macrocycle via cation–\( \pi \) interaction, which leads to the increase of the charge density of this Na-Zn-QDB complex. Second, the co-ions perform as a core to attract two macrocycles intermolecularly, which is like a \( \pi \)-Na\textsuperscript{+}–\( \pi \) sandwich trimer model. Therefore, if we only change the cations of the added electrolyte, the force of cation–\( \pi \) will change, while the other interactions keep similar, and the variations of the distance between each Zn-QDB macrocycle are opposite. For the first hypothesis, if the cation with larger affinity is added to the Zn-QDB solution, more cations will bind to the macrocycle. Consequently, the repulsion force among macrocycles will be increased by their relatively higher charge density, which results in the larger distance between each Na-Zn-QDB, that is, smaller assemblies (Scheme 1).

To check the hypotheses of the role of co-ions in the self-assembly process of Zn-QDB, that is, whether the cation–\( \pi \) binding acts as intramolecular or intermolecular, 0.5 mg mL\textsuperscript{-1} TMAI, NaI, and LiI solutions were titrated into the Zn-QDB solutions (1.0 mL 0.1 mg mL\textsuperscript{-1}) with the molar ratio of \( n_{\text{Na}}/n_{\text{Zn-QDB}} = 4:1 \), separately. Based on the well-studied binding enthalpies of cation–benzene interaction in the gas phase (\( \Delta H_{\text{TMA}} < \Delta H_{\text{Na}} < \Delta H_{\text{Li}} \))\textsuperscript{10b} and our previous work of cation–\( \pi \) interaction in DMSO solution (Na\textsuperscript{+} ion had stronger binding strength with pyrene than TMA\textsuperscript{+} ion),\textsuperscript{13b} the lithium ions are expected to have the strongest affinity to the conjugated \( \pi \) system of Zn-QDB in CH\textsubscript{3}CN solution. Until the system reached thermodynamic equilibrium, the \( R_h \) of formed assemblies was obtained. The \( R_h \) results showed that the average sizes of blackberries decrease with the stronger cation–\( \pi \) interaction, which supports the first hypothesis that the dominant role of the additional cations is intramolecularly captured by Zn-QDB with increased charge density, while the intermolecular attraction binding is minor (Figure 3a).

The relationship of co-ion effect via cation–\( \pi \) interaction and counterion effect via counterion-mediated attraction is also worth considering, because the cation–\( \pi \) interaction is one of the strongest noncovalent interactions and the counterion-mediated attraction has been proven as the major driving force in the blackberry formation. Herein, three sets of the NaI-Zn-
The mechanism of the binding process between Electrolytes and the Macrocycles. Isothermal titration calorimetry (ITC) is applied to elucidate the binding process. TMAI, NaI, and LiI solutions (0.25 mL, 1.2 mM) were titrated into the Zn-QDB (1.0 mL, 0.1 mM) solutions at 288 K, separately. These three experiments showed similar curve shape (Figures 3c and S7). With the injection of salt continuing, the first two injections were exothermal processes. After the third injection, the binding process began to absorb heat, and the heating level from each individual peak first increased, followed by gradual decrease, finally reaching an almost saturated situation. From the ITC curve, two different phases indicate the co-existence of two binding processes, and their relative binding sites are nonidentical. The two processes can be attributed to the binding of the cations with the \( \pi \) system in Zn-QDB and the substitution of \([\text{NO}_3]^-\) around positively charged macrocycles by I\(^-\). Their binding sites are attributed to the exterior aromatic ligands and the Zn\(^{2+}\) nodes in the core of macrocycles, respectively. Moreover, the nonidentical binding processes match well with our conclusion that the counterion-mediated attraction while larger than \( \pi-\pi \) stacking. The assembly of highly ordered blackberry-type structures is mainly driven by the competition of cation–\( \pi \) interaction and counterion-mediated attraction among Zn-QDB macrocycles. The partially distributed enhanced \( \pi-\pi \) stacking helps stabilize the assembly structures.

In addition, the co-ion effect on the \( \pi-\pi \) stacking in the self-assembly process of Zn-QDB after introducing extra NaI is studied by UV–vis spectroscopy. Since the \( \pi-\pi \) stacking is a short-range attractive force existing when two macrocycles tightly close to each other and the blackberry-type assemblies are obviously softer than the crystal structures, the \( \pi-\pi \) stacking can exist in several oligomers which are partially distributed on the single layer of blackberries. In the previous experiments, the \( \pi-\pi \) stacking has been proven to have no significant contribution in the self-assembly of salt-free Zn-QDB solution. However, after introducing NaI, the UV–vis results showed a red shift at 428 nm with the discrete NaI-Zn-QDB transforming to blackberries; meanwhile, the absorptions at 280 and 367 nm had no obvious change (Figure 3b). The consistent absorption of ligands suggests that the tightly binding of Na\(^+\) with Zn-QDB is not affected by the assembly process. The red shift indicates that the \( \pi-\pi \) stacking is significantly increased by the addition of Na\(^+\) during the self-assembly process, and we speculate that the binding type is \( \pi-\pi \) tetramer model (Scheme 2). Consequently, we can conclude that the additional co-ions have a cooperative effect on the \( \pi-\pi \) stacking.

Furthermore, the contribution of the enhanced \( \pi-\pi \) stacking could also be examined. If the contribution of the \( \pi-\pi \) stacking is greater than the cation–\( \pi \) interaction, then the effect of the enhanced attractive forces would be more dominant than the effect of the increased repulsion due to the increase of the charge density. Therefore, the increase of the attractive forces leads to a smaller curvature of the spherical shell, which results in larger blackberry sizes. In our cases, the \( \pi-\pi \) stacking should be more enhanced by the Li\(^+\) than the Na\(^+\) or TMA\(^+\). As a result, the LiI-Zn-QDB assembly structures should have the largest sizes. Nevertheless, the experiments showed an obvious opposite result. Hence, we can draw a conclusion that the enhanced \( \pi-\pi \) stacking owns the minimum contribution on the self-assembly. In brief, three forces are involved in the self-assembly process of Zn-QDB after the addition of extra salts, and the contribution from cation–\( \pi \) interaction is smaller than counterion-mediated attraction while larger than \( \pi-\pi \) stacking.

The thermodynamic parameters of the interactions between Zn-QDB and three iodide salts can be further obtained by calorimetry (ITC) applied to elucidate the binding process. TMAI, NaI, and LiI solutions (0.25 mL, 1.2 mM) were titrated into the Zn-QDB (1.0 mL, 0.1 mM) solutions at 288 K, separately. These three experiments showed similar curve shape (Figures 3c and S7). With the injection of salt continuing, the first two injections were exothermal processes. After the third injection, the binding process began to absorb heat, and the heating level from each individual peak first increased, followed by gradual decrease, finally reaching an almost saturated situation. From the ITC curve, two different phases indicate the co-existence of two binding processes, and their relative binding sites are nonidentical. The two processes can be attributed to the binding of the cations with the \( \pi \) system in Zn-QDB and the substitution of \([\text{NO}_3]^-\) around positively charged macrocycles by I\(^-\). Their binding sites are attributed to the exterior aromatic ligands and the Zn\(^{2+}\) nodes in the core of macrocycles, respectively. Moreover, the nonidentical binding processes match well with our conclusion that the counterion-mediated attraction performs more dominantly in the assembly process.

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Figure 3. (a) Average $R_h$ values of the blackberries formed by 0.1 mg mL$^{-1}$ Zn-QDB with additional 4 equiv of TMAI, NaI, and LiI in CH$_3$CN, measured by DLS. (b) Time-resolved UV–vis spectra of Zn-QDB (32 μM) in CH$_3$CN with the addition of 4 equiv of NaI. The inset shows the red shift of peak position from 428 to 450 nm. (c) ITC results: 250 μL 4.8 mM NaI was titrated into 1.0 mL of 0.1 mM Zn-QDB in CH$_3$CN. (d) Fitting of the second phase of titration curve by an independent model.

Scheme 2. Schematic Illustration of Why the Counterion-Mediated Attraction Is the Major Driving Force$^a$

"Upper: If the cation–π interaction is more dominant, the repulsion will increase leading to smaller blackberry sizes. Middle: Salt-free control experiment. Lower: If counterion-attraction is more dominant, then the attraction will increase leading to larger blackberry sizes. The red rectangle frame represents the π-Na$^+-π$ π tetramer model."
fitting these ITC curves. Since both ion-pair formation and cation–π binding are exothermic processes, the significant heat absorptions (ΔH > 0) are attributed to the destruction of solvation shell accompanied by the binding process. Therefore, the transition point at the sixth injection (Figure 3c) represents that the decay rate of the endothermal process is equal to the rate of the two exothermic processes. Consequently, after the transition point, the binding between I− and Zn-QDB is still more dominant, while the binding sites of aromatic ligands are almost saturated by Na+. It is difficult to fit the whole process because the situation in the first phase is complicated. However, the data obtained from the last phase can be well fitted by the independent model, and the binding constant (Kb) of I− with Zn-QDB is obtained from the fitting results (Table 1). The results indicate the iodine ions have the largest affinity with Zn-QDB in the presence of TMA+, which is in agreement with the earlier conclusion that TMAI-Zn-QDB has the lowest charge density and the fact that TMAI-Zn-QDB forms the largest blackberries.

### 3. CONCLUSION

In summary, we provide new insights into the strong co-ion effects on the solution behaviors of macrocation Zn-QDB, which can self-assemble into highly ordered blackberry-type structures. During the assembly process, the additional cationic co-ions could be captured by the aromatic rings on the outer sphere of the positively charged macroion via cation–π interaction. This intramolecular binding leads to a higher charge density of macroion. The stronger the cation–π binding force is, the higher the charge density Zn-QDB will carry, and the smaller the assembly sizes will be. In the macroion solution with extra electrolytes, three binding forces including counter-ion interaction, cation–π interaction, and π–π stacking are involved, and their contribution sequence is revealed through the variation of blackberry sizes, the lag phase of assembly process, as well as the absorbance curves in UV–vis spectra, and the order is counterion-mediated attraction > cation–π interaction > π–π stacking. The experimental results show the competition relationship between the co-ion effect and the counterion effect. Moreover, the co-ion effects via cation–π interaction cooperatively strengthen the intermolecular π–π stacking which “glues” the macrocycles together and thus contributes to the stability of whole assembly structures.

### 4. EXPERIMENTAL SECTION

#### 4.1. Synthesis of Zn-QDB

The Zn-QDB was synthesized by the modification of reported procedure.125Zn(NO3)2·6H2O (30 mg, 0.10 mmol) and QDB (70 mg, 0.10 mmol) were dissolved in CH3OH/CH2Cl2 (2:10 in volume) to give a light-yellow solution. Yellow crystals were obtained after standing the solution for several days at room temperature. The crystals were filtered and used for preparing the experiment solutions.

#### 4.2. Static Light Scattering

A commercial Brookhaven Instrument LLS spectrometer equipped with a solid-state laser operating at 532 nm was used for measurement of both SLS and DLS. SLS experiments were performed at scattering angles (θ) between 20° and 105°, at 2° intervals. However, due to the large fluctuations in scattered intensities at low scattering angles, we removed the data from 20° to 40° in the final analysis. Derived from the Rayleigh–Gans–Debye equation, a partial Zimm plot was used to analyze the SLS data to obtain the radius of gyration (Rg). The partial Zimm plot stems from the following approximate formula: \(1/I = C(1 + R_g^2 (q^2/3))\). Here \(R_g\) is determined from the slope and the intercept of a plot of \(1/I\) vs \(q^2\).

#### 4.3. Dynamic Light Scattering

DLS measures the intensity–intensity time correlation function by means of a BI-9000AT multichannel digital correlator. The field correlation function \(g(1)(r(t))\) was analyzed by the constrained regularized CONTIN method to yield information on the distribution of the characteristic line width \(Γ\). The normalized distribution function of the characteristic line width, \(G(Γ)\), so obtained, can be used to determine an average apparent translational diffusion coefficient, \(D_{app} = Γ / q^2\), where \(q\) is the scattering factor. The hydrodynamic radius \(R_h\) is related to \(D\) via the Stokes–Einstein equation: \(R_h = kT/(6πη \cdot D)\), where \(k\) is the Boltzmann constant and \(η\) the viscosity of the solvent at temperature \(T\). From DLS measurements, the particle-size distribution in solution is obtained from a plot of \(Γ G(Γ)\) vs \(R_h\).

#### 4.4. Isothermal Titration Calorimetry

A commercial TA Instruments Nano ITC standard volume isothermal titration calorimeter was applied to conduct the measurements. 1.0 mg mL−1 of Zn-QDB solution was placed in a 1.1 mL calorimetric cell. Twelve mM LiI, 12 mM NaI, and 12 mM TMAI were used to titrate the sample solution, respectively. The Zn-QDB solution was injected into the calorimetric cell with a clean syringe, and the salt solution was loaded into a 250 μL calorimetry syringe. The temperature of the cell was set at 15 °C. The injection volume was set at 10 μL each time. A 300 s delay was used between each injection. The solution was mixed at 250 rpm. The heat of dilution for each salt (background heat) was performed with the same concentration of salt that was used for the Zn-QDB solutions only with 1.1 mL anhydrous CH3CN in the cell instead of Zn-QDB solution.

#### 4.5. Other Characterizations

UV–vis spectra were measured using a Lambda 45 UV–vis spectrometer (PerkinElmer Instruments). The solution fluorescence spectra were measured on a JASC0 FP-6500. The TEM images were taken on a JEOL-1230 electron microscope with an accelerating voltage of 120 kV. Samples for the TEM analysis were prepared by dropping a small volume of the solution sample onto a holey carbon film on copper grid. 1H NMR measurements in the liquid state were performed on a Bruker Avance 500 spectrometer equipped with a 5 mm triple-axis gradient (TXI) probe. ESI-MS was carried out on an HPLC-Q-Tof mass spectrometer. AFM was conducted using a Bruker Dimension Icon in Scansyst mode with a Scansyst-Air cantilever (spring constant 0.2–0.8 N/m). Silicon substrates were cleaned using the well-known Piranha method followed by sonication in DI water for 15 min. Samples were spin coated onto the silicon wafer and left to dry under ambient condition.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b06564.

Detail of molecule structure of Zn-QDB, ESI-MS spectra, conductivity experiment result, 1H NMR titration results, fluorescent spectra, light-scattering results, AFM results, ITC results (PDF).

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