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Supporting Information

Indole-based aerogel for enhanced removal of heavy metals from water via the synergistic effects of complexation and cation−π interaction

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Characterization

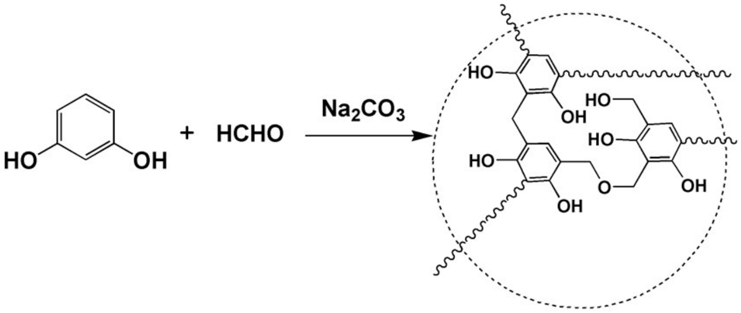
For zeta potential measurements, 0.1 g of each of RFA and 4-HIFA powder was suspended in the 5 mL of deionized water. The Zetasizer Nano ZS particle characterization system from Malvern Instruments, equipped with an MPT-2 automatic titrator and titration media degasser, was used to measure the zeta potential (ξ) at pH = 6. Zeta potential was determined from the electrophoretic mobility (u) based on Smoluchowski's formula. Before measurement, each of the test samples was first mixed for 5 s prior to transferring it to the Malvern polystyrene U-shaped cell. Subsequently, samples were stabilized at 25 °C for 5 s, and each of the measurements was conducted at 25 °C and repeated 10 times.[1] The 0.1 M solutions of sodium hydroxide (NaOH) and hydrochloric acid (HCl) solutions were used as a titration media to automatically adjust the pH values. Charge densities of both RFA and 4-HIFA were measured using a colloidal titration method. In the colloidal titration, RFA and 4-HIFA were titrated with standard cationic polyelectrolyte [poly (diallyldimethyl ammonium chloride) (poly-DADMAC)] (concen-tration = 0.714 mN) and standard anionic polyelectrolyte [polyvinyl sulfate (PVSK)] (concentration = 1.0214 mN), respectively, which are widely used as the cationic and anionic reactants in colloidal titration.[2] The end point was determined using Mütek PCD 03 Particle Charge Detector (Herrsching, Germany). Three repeatetests were conducted to obtain an average value for each sample. The contact angle of aerogel was measured by optical contact angle measuring instrument (Kruss DSA10).

Treating the real sewage by 4-HIFA

The sewage containing Zn^{2+}, Cd^{2+}, Cu^{2+} and Ni^{2+} used in this study is obtained from a metals smeltery located in Mianyang, Sichuan, China. The sewage is collected and stored in a refrigerator at -4 ^{o}C. The quality of sewage in Table S10 shows high contents of Na^{+}. Prior to the experiment, the sewage is treated using a filter membrane (0.45 mm) to remove the impurity phase. An amount of 0.04 g 4-HIFA was added into the 50 mL sewage undergoing vigorous stirring continuously for 5 min, 30 min, 1 h, 2 h, 3 h, 4 h and 5 h.

Preparation of resorcinol-formaldehyde aerogel (RFA)

The RFA was prepared by mixing resorcinol with formaldehyde in deionized water in a molar ratio of 1 : 2. The total solid content in the pre-gelsolution was kept at 20%. Sodium carbonate was used as catalyst with the molar ratio of resorcinol : Na_2CO_3 = 50 : 1. And the above solution was stirred for 20 min, then poured into ampoule bottles, followed by heat treatment at 80 °C for 24 h and was capable of gelling. Before supercritical drying, water in wet gel was replaced by solvent exchange with acetone for three times once in 24 h. After that, the gel was supercritical dried at 45 ^{o}C for 7 days and RFA was obtained, finally.



Scheme S1. Preparation scheme of resorcinol-formaldehyde aerogel (RFA).

Table S1. Characteristics of the 4-HIFA and RFA.

Parameters	RFA	4-HIFA
Zeta potential [mV]	-7.1	-10.5
Charge density [meq/g]	−0.314	-0.458
Contact angle [°]	5	9

Table S2. Kinetics data of Cu^{2+} using 4-HIFA.

C_0 [ppm][a)]	Time (min)	C_f [ppm]	Removal [%]	K_d [mL g^{-1}]
10.67	5	0.240	97.75	5.4×10^4
	30	0.117	98.90	1.1×10^5
	60	0.051	99.52	2.6×10^5
	120	0.036	99.66	3.7×10^5
	180	0.016	99.85	8.3×10^5
	240	0.012	99.89	1.1×10^6
	300	0.010	99.91	1.3×10^6

a)m = 0.04 g, V = 50 mL, V/m = 1250 mL g^{-1}, pH value: 6.0.

Table S3. Kinetics data of Cr^{3+} using 4-HIFA.

C_0 [ppm][a)]	Time (min)	C_f [ppm]	Removal [%]	K_d [mL g^{-1}]
9.81	5	0.446	95.45	2.6×10^4
	30	0.380	96.13	3.1×10^4
	60	0.324	96.70	3.7×10^4
	120	0.286	97.08	4.2×10^4
	180	0.265	97.30	4.5×10^4
	240	0.250	97.45	4.8×10^4
	300	0.246	97.49	4.9×10^4

a)m = 0.04 g, V = 50 mL, V/m = 1250 mL g^{-1}, pH value: 6.0.

Table S4. Kinetics data of Zn^{2+} using 4-HIFA.

C_0 [ppm][a)]	Time (min)	C_f [ppm]	Removal [%]	K_d [mL g^{-1}]
10.10	5	0.344	96.59	3.5×10^4
	30	0.283	97.20	4.3×10^4
	60	0.221	97.81	5.6×10^4
	120	0.187	98.15	6.6×10^4
	180	0.165	98.37	7.5×10^4
	240	0.150	98.51	8.3×10^4
	300	0.140	98.61	8.9×10^4

a)m = 0.04 g, V = 50 mL, V/m = 1250 mL g^{-1}, pH value: 6.0.

Table S5. Kinetics parameters (pseudo-second-order-model) for adsorbing metal ions onto 4-HIFA.

Ions	$q_{e,exp}$	k_2	$q_{e,cal}$(mg/g)	R^2
Ni^{2+}	12.24	0.270	12.24	1
Cu^{2+}	13.33	0.290	13.34	1
Cr^{3+}	11.96	0.200	11.96	1
Zn^{2+}	12.45	0.187	12.45	1

Table S6. Sorption data of 4-HIFA toward Cu^{2+}.

C_0 [ppm][a)]	C_f [ppm]	Removal [%]	q_m [mg g^{-1}]	K_d [mL g^{-1}]
10.67	0.05	99.53	13.3	2.7×10^5
52.7	0.34	99.35	65.5	1.9×10^5
104	1.21	98.84	128.5	1.1×10^5
209	15	92.82	242.5	1.6×10^4
345	144	58.26	251.3	1.7×10^3
508	296	41.73	265.0	9.0×10^2

[a)] m = 0.02 g, V = 25 mL, V/m = 1250 mL g^{-1}; contact time: 24 h; pH value: 6.0.

Table S7. Sorption data of 4-HIFA toward Cr^{3+}.

C_0 [ppm][a)]	C_f [ppm]	Removal [%]	q_m [mg g^{-1}]	K_d [mL g^{-1}]
9.81	0.32	96.74	11.9	3.7×10^4
47.8	6.3	86.82	51.9	8.2×10^3
96	34	64.58	77.5	2.3×10^3
214	147	31.31	83.8	5.7×10^2
359	289	19.50	87.5	3.0×10^2
499	425	14.83	92.5	2.2×10^2

[a)] m = 0.02 g, V = 25 mL, V/m = 1250 mL g^{-1}; contact time: 24 h; pH value: 6.0.

Table S8. Sorption data of 4-HIFA toward Zn^{2+}.

C_0 [ppm][a)]	C_f [ppm]	Removal [%]	q_m [mg g^{-1}]	K_d [mL g^{-1}]
10.1	0.28	97.23	12.3	4.4×10^4
53	5.1	90.38	59.9	1.2×10^4
103	34	66.99	86.3	2.5×10^3
211	112	46.92	123.8	1.1×10^3
349	252	27.79	121.3	4.8×10^2
509	409	19.65	125.0	3.1×10^2

[a)] m = 0.02 g, V = 25 mL, V/m = 1250 mL g^{-1}; contact time: 24 h; pH value: 6.0.

Table S9. Adsorption constants of Langmuir models for the adsorption of Ni^{2+}, Cu^{2+}, Cr^{3+} and Zn^{2+} ions onto 4-HIFA.

Ions	q_m (mg/g)	b (L/mg)	R^2
Ni^{2+}	240.4	0.4468	0.9997
Cu^{2+}	264.6	0.5324	0.9993
Cr^{3+}	92.2	0.1401	0.9981
Zn^{2+}	126.6	0.1384	0.9987

Table S10. Characteristics of sewage.

Parameters	Unit	Value
pH	–	6.8 ± 0.2
Zn^{2+}	mg/L	152 ± 3
Cd^{2+}	mg/L	90 ± 2
Cu^{2+}	mg/L	60 ± 1
Pb^{2+}	mg/L	< 0.1
Fe^{3+}	mg/L	< 1.0
Cr^{3+}	mg/L	<0.5
Ni^{2+}	mg/L	70 ± 2
Na^{+}	mg/L	1800 ± 100
Ca^{2+}	mg/L	200 ± 10
Mg^{2+}	mg/L	150 ± 6

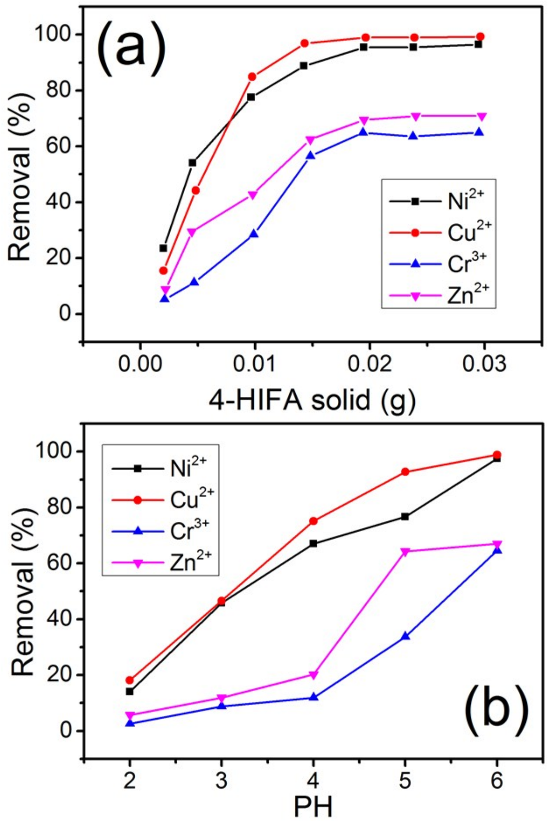


Figure S1. (a) The amount of 4-HIFA effect on the removal of Ni^{2+}, Cu^{2+}, Cr^{3+} and Zn^{2+} (C_0 = 100 mg/L; V = 25 mL; pH value: 6.0; contact time: 24 h), (b) PH effect on the removal of Ni^{2+}, Cu^{2+}, Cr^{3+} and Zn^{2+} by 4-HIFA (C_0 = 100 mg/L; m = 0.02 g, V = 25 mL, V/m = 1250 mL g^{-1}; contact time: 24 h).

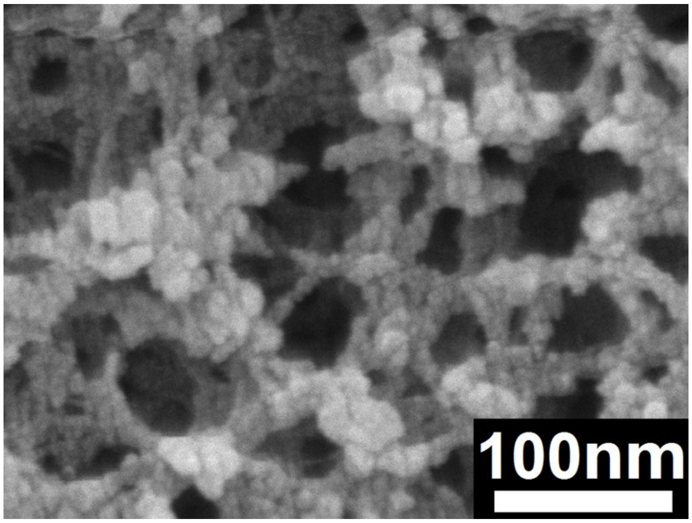


Figure S2. SEM image of 4-HIFA.

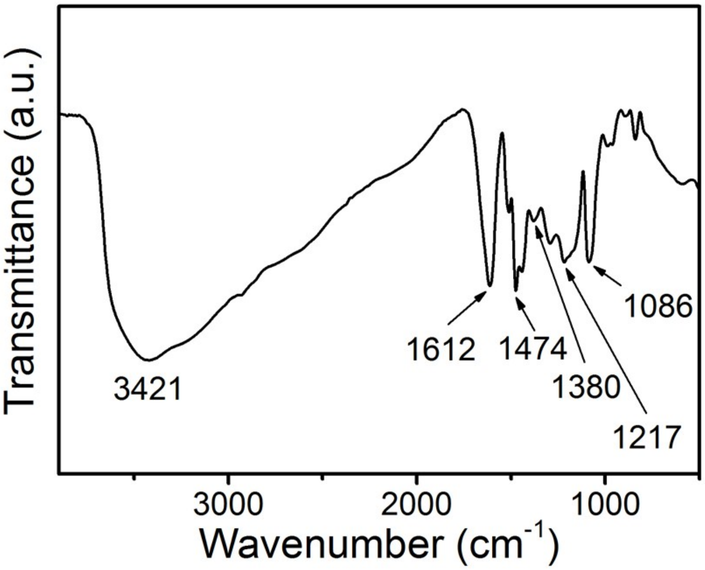


Figure S3. IR spectrum of RF aerogel (RFA).

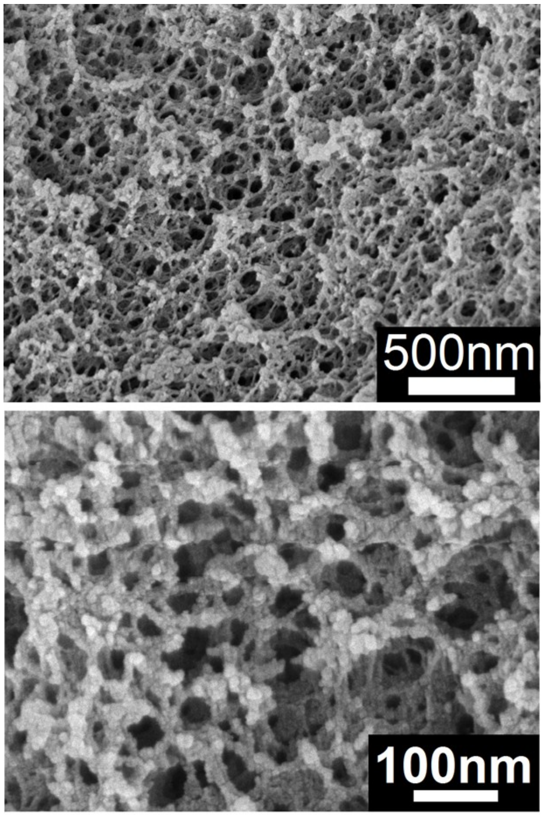


Figure S4. SEM images of RF aerogel (RFA).

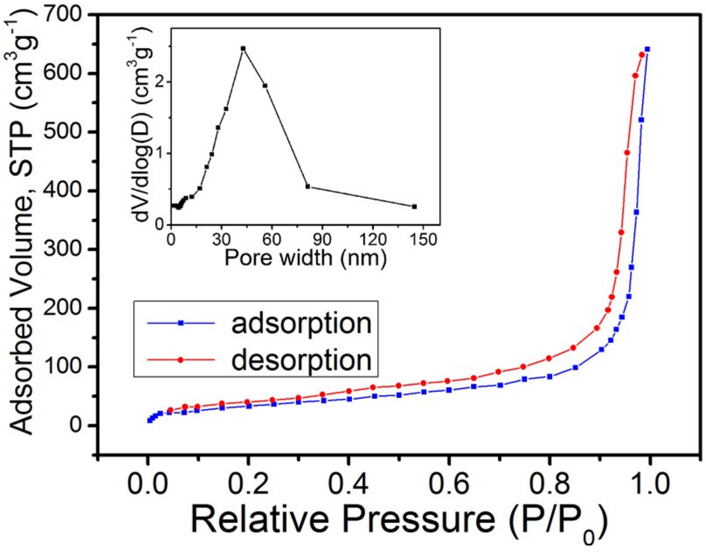


Figure S5. Nitrogen adsorption – desorption isotherms and the pore size distribution (inset) of RF aerogel (RFA). The BET specific surface area of RF aerogel was estimated to be 151 m^2 g^{-1}, the pore size was distributed at 40 nm.

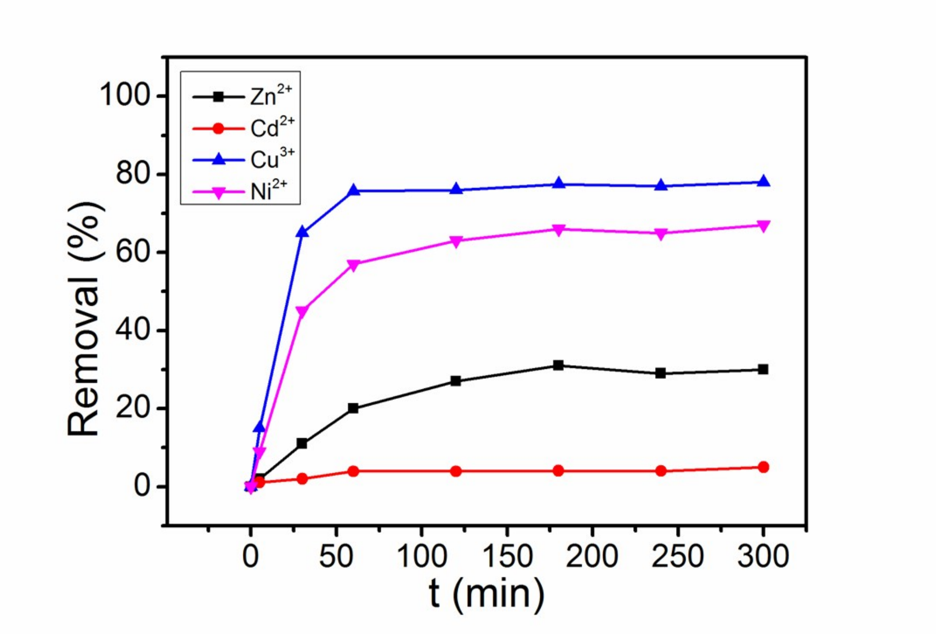


Figure S6. Zn^{2+}, Cd^{2+}, Cu^{2+} and Ni^{2+}sorption kinetics over 4-HIFA used to treat the real sewage.

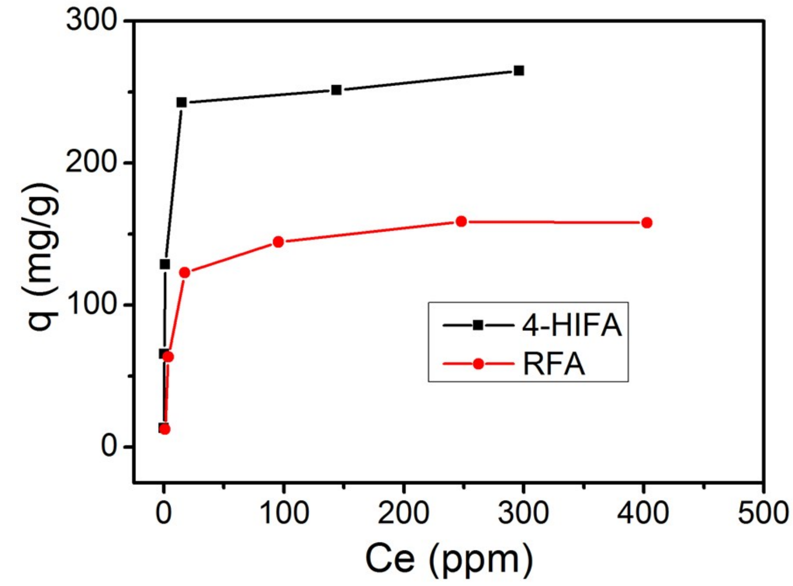


Figure S7. Cu^{2+} aqueous solution adsorption isotherms for indole-based aerogel (4-HIFA) and RF aerogel (RFA).

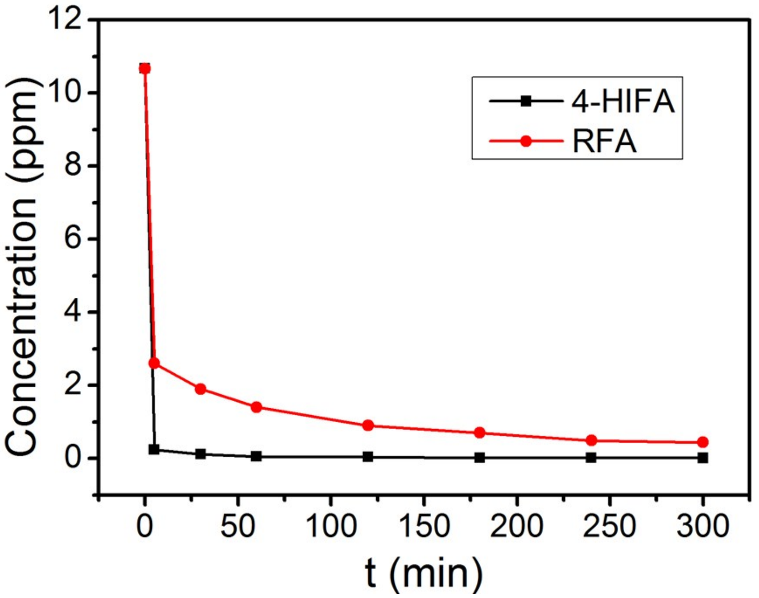


Figure S8. Cu^{2+} sorption kinetics over indole-based aerogel (4-HIFA) and RF aerogel (RFA).

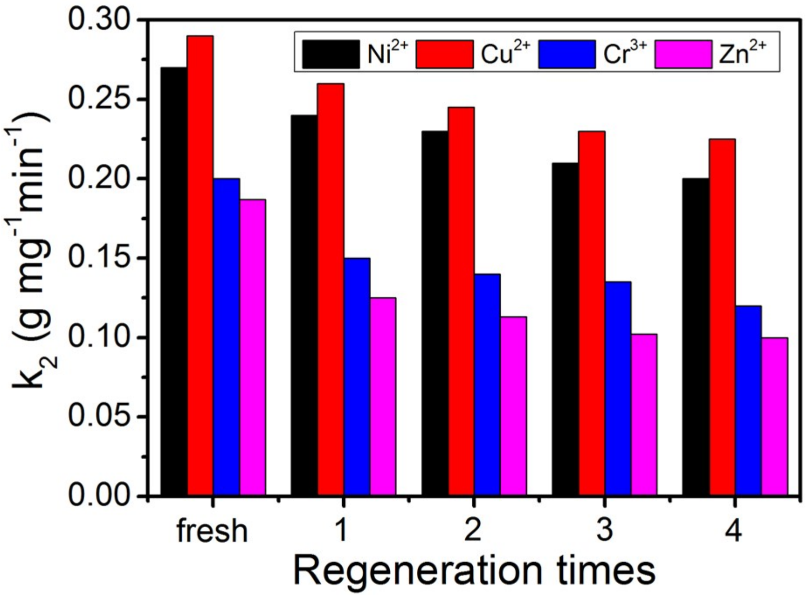


Figure S9. Adsorption equilibrium rate constants (k_2) (C_0 = 10 mg L^{-1}; m = 0.04 g, V = 50 mL, V/m = 1250 mL g^{-1}; pH = 6) of metal ions on 4-HIFA after repeated adsorption cycle (treated by 1 mol L^{-1} HCl).

Simulation Method

Molecular dynamics (MD) MD simulation was performed using the amorphous cell module of Materials Studio (Accelrys Software Inc.) with a dreiding force field whose intermolecular parameters were optimized using quantum mechanics. A parent 4-HIFA (as described in Scheme 1 in the main text) with a five-generation dendrimer was built that consists of indole and hydroxyl groups. Although size of the parent 4-HIFA chain is not sufficiently long to represent conformations of a real polymer chain, a previous study has reported a good agreement between experiments and simulations when simulated Li-CMP chains are short (merely five-generation dendrimer on average).[3] Moreover, a periodic boundary condition were imposed and an initial density of 0.9 g/cm^3 was used to simulate the polymer conformation in bulk under an equilibrium state. The 4-HIFA dendrimer in simulation box was relaxed through NVT for 1 ns at 800 K with time steps of 0.2 fs. The simulation of high-temperature relaxation was closely followed a protocol S9 suggested previously.[4] After 1 ns of simulated relaxation at 800 K, the system temperature is decreased to 273 K. In order to obtain a suitable structure for further analysis, ten different initial structures for each system were built and relaxed according to the procedure mentioned previously. The one with the lowest system energy was selected as the MD result for further analysis. The MD simulation was performed to analyze the conformation of the complex between 4-HIFA and metal ions under an equilibrium state. For example, it is clear that the M^+ cation is close to an indole group. To see this in a quantitative way, the radial distribution function, $g_{AB}(r)$, was introduced to describe how density of designated particles varies as a function of distance from a reference particle. Usually, $g_{AB}(r)$ is determined by measuring the ensemble averaged distance between all particle pairs, as follows,

$$g_{AB}(r) = \frac{\langle n_{AB}(r) \rangle}{4\pi r^2 \Delta\rho_{AB}} \quad \square \; \square \; \square \; \square \; \square$$

where, $n_{AB}(r)$ is the distance of each pair between A (M^+) and B (indole) in the simulation box. <...> represents an ensemble average. $\Delta\rho_{AB}$ is the rate of change in the average number density of M^+ over distance from an indole ring. The plot of $g_{AB}(r)$ gives the local density of B around A at a distance r. $g_{AB}(r) = 1$ indicate the particles are completely uncorrelated. A positive peak of $g_{AB}(r)$ reflects a definite correlation between atoms at r. In addition, the complexation also confirmed by the same calculation methods.

Density functional theory (DFT) The molecules were optimized with density functional theory (DFT) at the M062x/6-311+g** level theory, using the Gaussian-09 package. The electrostatic potential (ESP) of the model were analyzed using Multiwfn 3.3.5.[5] The simulation procedure was closely followed a previously suggested one.[6]

References

(1) D. Zheng, N. Wang, X. Wang, Y. Tang, L. Zhu, Z. Huang, H. Tang, Y. Shi, Y. Wu and M. Zhang, *J. Hazard. Mater.*, **2012**, 199, 426.

(2) K. Ueno, *J. Chem. Educ.*, **1985**, 62, 627.

(3) A. Li, R.-F. Lu, Y. Wang, X. Wang, K.-L. Han, W.-Q. Deng, *Angew. Chem. Int. Ed.,* **2010**, *49*, 3330.

(4) K. J. Lee, W. L. Mattice, R. G. Snyder, *J. Chem. Phys.,* **1992**, *96*, 9138.

(5) T. Lu, F. Chen, *J. Comput. Chem.,* **2012**, *33*, 580.

(6) T. Lu, F. Chen, *J. Mol. Graph. Model.,* **2012**, *38*, 314.