Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Material for:

Tuning Cation-Binding Selectivity and Capacity via Side Chain-Dependent Molecular Packing in Solid State

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General Remarks

All the chemicals were obtained from commercial suppliers and used as received unless otherwise noted. Aqueous solutions were prepared from MiliQ water. ICP data were recorded on Thermo Fisher X Series 2. Transmission electron microscopy (TEM) images were recorded on JEOL 3010 microscope equipped with energy-dispersive X-ray spectroscopy. Scanning electron microscopy (SEM) images were recorded on a JEOL JSM-5200 Microscope. Powder XRD patterns were recorded on a Bruker D8 Avance diffractometer using Cu radiation (λ = 1.5406 Å).

Preparation of the Nanofibers and Nanoplates

The nanofibers, nanosheets and nanoplates formed by pentamers **1-3** were prepared by slow diffusion of varying solvents such as ethyl acetate into pentamer-containing DMSO solution. Typically, 1 mg of pentamer was dissolved in 0.4 mL of DMSO to prepare a clear solution, which was then transferred to a NMR tube. 100 μL of DMSO was added onto the top of this sample-containing DMSO solution with the remaining part of the NMR tube filled with various organic solvents. 2-4 weeks later, the slowly formed fibers, sheets or plates were transferred into an eppendorf tube and centrifuged. The supernatant was decanted and solid residue was washed with ethyl acetate and centrifuged three times. 1 mL of ethyl acetate was then added into the tube to re-suspend the fibers.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

For ICP measurement, the concentration of each metal ion is set constant at 0.10 mM in H_2O containing 1% HNO_3, and that of macrocyclic hosts **1** is set to be at [host]:[total metal ion] = 1 or 1:5. Extractions were carried out in a biphasic liquid-solid method, which involves shaking the suspended solid in aqueous solution for 24 hours at 25 ^{o}C. After filtration of the aqueous solution using 0.45 um syringe filter, the concentration of the residual ions in the aqueous layer was measured and referred to as C_1. The control experiments using $CHCl_3$ containing no organic host were also carried out at 25 ^{o}C. After filtration of the aqueous solution using 0.45 um syringe filter, the concentration of the residual ions in the aqueous layer was measured and referred to as C_2. A difference between C_2 and C_1 is divided by the original concentration of the ion to yield the extraction efficiency. All the reported data are averaged values over six runs with relative errors within 2%, and only extraction efficiencies of $\geq$ 2% are listed.

Table S1 Extraction efficiencies (%) of 18 metal ions by nanostructured **1-3** as determined by inductively coupled plasma mass spectrometry (ICP).

		Na^+	K^+	Rb^+	Cs^+	Ba^{2+}	Cu^{2+}	Ag^+	Hg^{2+}	Pb^{2+}	Li^+, Mg^{2+}, Ca^{2+}, Al^{3+}, Mn^{2+}, Fe^{3+}, Ni^{2+}, Zn^{2+}, Cd^{2+}	**Total Extraction**[c]
1[a]	Dioxane	10	11	8	**28**	7	-	-	13	-	-	77
	Ethyl Acetate	12	9	7	29	11	-	-	**43**	-	-	111
	Ethanol	3	11	9	**29**	13	-	-	12	-	-	77
	Acetone	7	4	3	17	4	-	-	**29**	-	-	64
	Acetonitrile	9	3	-	6	4	-	-	**40**	-	-	62
	Ether	5	7	-	9	4	-	-	**19**	-	-	44
	Tetrahydrofuran	9	3	5	17	8	-	-	**37**	-	-	79
	Powder form	3	5	-	-	-	-	18	6	-		
2[a]	Dioxane	8	**15**	-	-	-	3	7	5	-	-	38
	Ethyl Acetate	**11**	**9**	-	-	-	-	**11**	5	-	-	36
	Ethanol	**8**	**9**	-	4	-	3	5	-	3	-	32
	Acetone	5	12	-	4	-	-	**24**	**23**	4	-	72
	Acetonitrile	6	5	-	-	-	-	8	**14**	-	-	33
	Ether	10	7	-	5	3	-	**14**	11	3	-	53
	Tetrahydrofuran	5	**13**	3	8	5	4	6	-	4	-	48
	Powder form	3	4	4	7	4	4	13	10	3		
3[a]	Dioxane	10	13	>99	> 99	97	11	92	76	86	-	583
	Ethyl Acetate	6	9	> 99	> 99	> 99	12	89	79	90	-	582
	Ethanol	13	7	> 99	> 99	> 99	18	95	84	97	-	611
	Acetone	11	12	> 99	> 99	> 99	5	90	83	93	-	591
	Acetonitrile	10	16	> 99	> 99	98	11	95	78	90	-	596
	Ether	9	9	> 99	> 99	> 99	15	94	86	97	-	607
	Tetrahydrofuran	9	11	> 99	> 99	> 99	4	74	74	73	-	542
	Powder form	-	-	80	98	72	4	15	13	8		
2[b]		86	> 99	>99	> 99	> 99	52	85	60	94	**Ca^{2+}** (55)	828

[a] The concentration of each metal ion in H_2O is set constant at 0.10 mM, producing a total concentration of 1.80 mM for 18 metal ions. Nanostructured organic hosts formed from seven solvents shown in Fig. 2 were added at [host]:[total metal ion] = 1:1, followed by shaking the biphasic water–solid system for 24 hours at 25 °C. Ion extractions from aqueous phase to suspended solid were monitored by measuring the residual concentrations of various metal ions in H_2O layer. Relative errors of ≤ 2% were obtained after averaging the data over 6 run, and only extraction efficiencies of ≥ 2% are listed. Metal nitrates were used for all metal ions.

[b] A chloroform solution containing host **2** at 1.80 mM was added into an aqueous solution containing 18 metal ions at [total metal ion] = 1.80 mM ([host]:[total metal ion] = 1:1). After shaking the biphasic water–$CHCl_3$ system for 24 hours at 25 °C. ion extractions from aqueous phase to suspended solid were monitored by measuring the residual concentrations of various metal ions in H_2O layer.

[c] The sum of extraction percentages involving all the extractable ions.

Table S2 Extraction efficiencies (%) of 18 metal ions by nanostructured **1**-**3** as determined by inductively coupled plasma mass spectrometry (ICP).

		Na^+	**K^+**	**Rb^+**	**Cs^+**	**Ba^{2+}**	**Cu^{2+}**	**Ag^+**	**Hg^{2+}**	**Pb^{2+}**	**Li^+, Mg^{2+}, Ca^{2+}, Al^{3+}, Mn^{2+}, Fe^{3+}, Ni^{2+}, Zn^{2+}, Cd^{2+}**	**Total Extraction[c]**
3[a]	Dioxane	4	11	28	70	24	-	7	-	4	-	148
	Ethyl Acetate	-	10	43	81	25	-	11	-	7	-	177
	Ethanol	7	-	29	69	25	-	7	-	4	-	141
	Acetone	6	13	19	50	21	-	8	-	6	-	123
	Acetonitrile	-	7	36	73	18	-	11	-	5	-	150
	Ether	5	9	36	78	28	-	8	-	5	-	169
	Tetrahydrofuran	-	8	37	75	28	-	10	-	6	-	164
2[b]		14	74	47	97	90	8	23	17	-	**Ca^{2+}** (10)	380

[a] The concentration of each metal ion in H_2O is set constant at 0.10 mM, producing a total concentration of 1.80 mM for 18 metal ions. Nanostructured organic hosts formed by **3** from seven solvents shown in Fig. 2 were added at [host]:[total metal ion] = 1:5, followed by shaking the biphasic water–solid system for 24 hours at 25 ^oC. Ion extractions from aqueous phase to suspended solid were monitored by measuring the residual concentrations of various metal ions in H_2O layer. Relative errors of ≤ 2% were obtained after averaging the data over 6 run, and only extraction efficiencies of ≥ 2% are listed. Metal nitrates were used for all metal ions.

[b] A chloroform solution containing host **2** at 0.54 mM was added into an aqueous solution containing 18 metal ions at [total metal ion] = 1.80 mM ([host]:[total metal ion] = 1:3.3). After shaking the biphasic water–$CHCl_3$ system for 24 hours at 25 ^oC. ion extractions from aqueous phase to suspended solid were monitored by measuring the residual concentrations of various metal ions in H_2O layer.

[c] The sum of extraction percentages involving all the extractable ions.

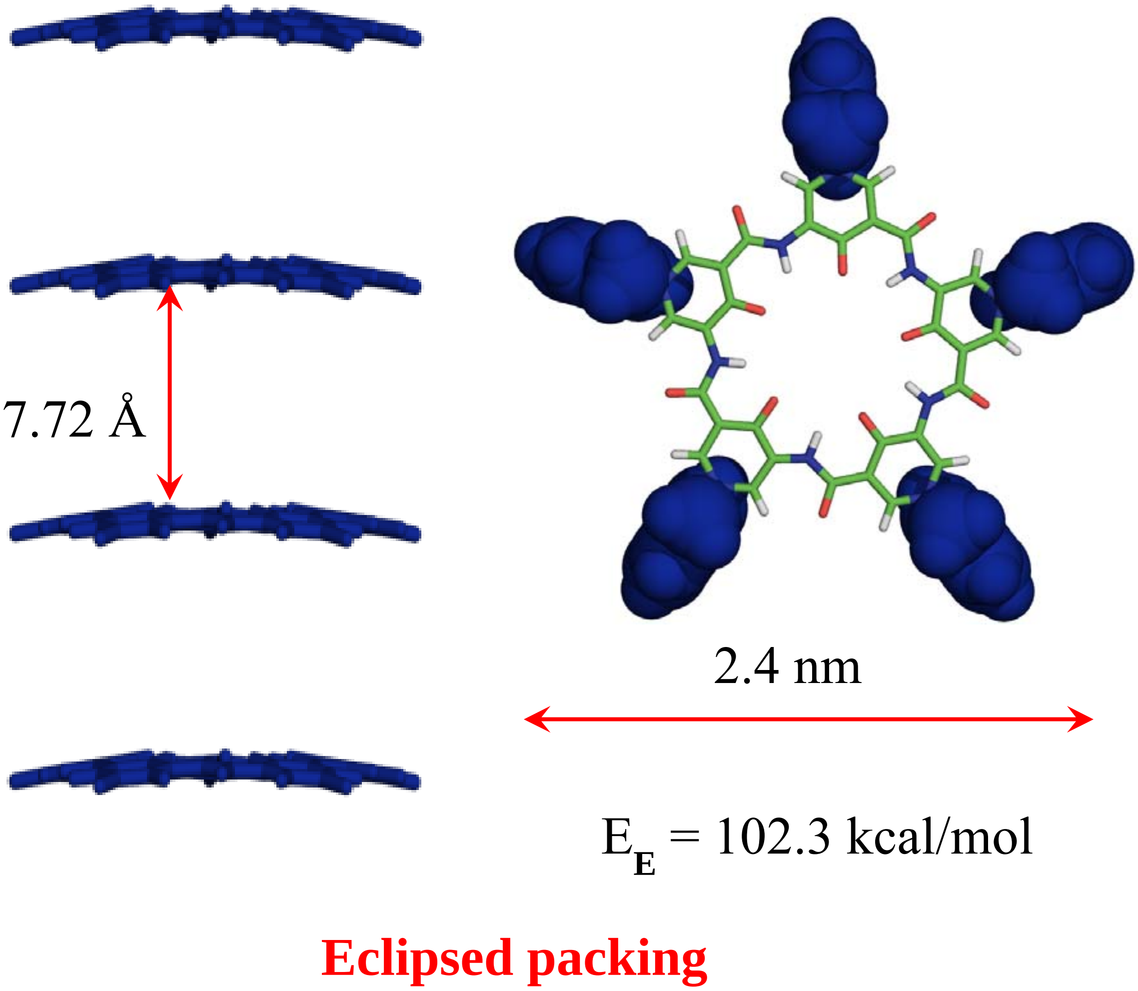

Figure S1. Computationally determined eclipsed packing by **3** and the corresponding energy normalized based on the most stable twisted packing.

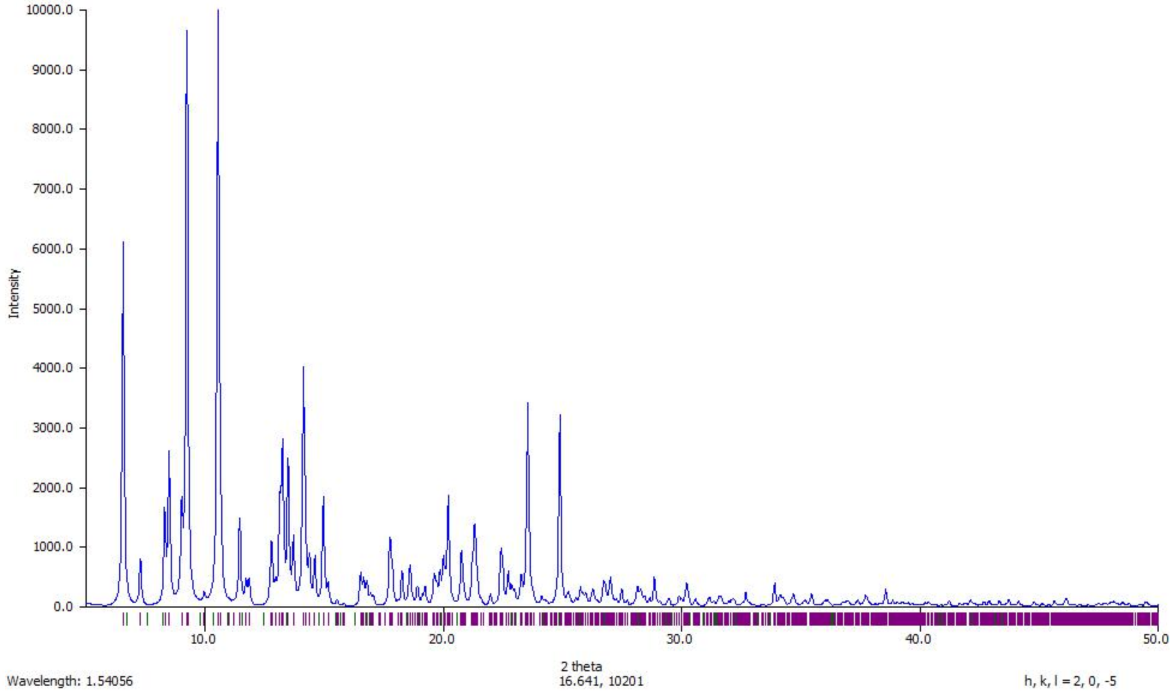

Figure S1. XRD pattern of single crystals of **3**.

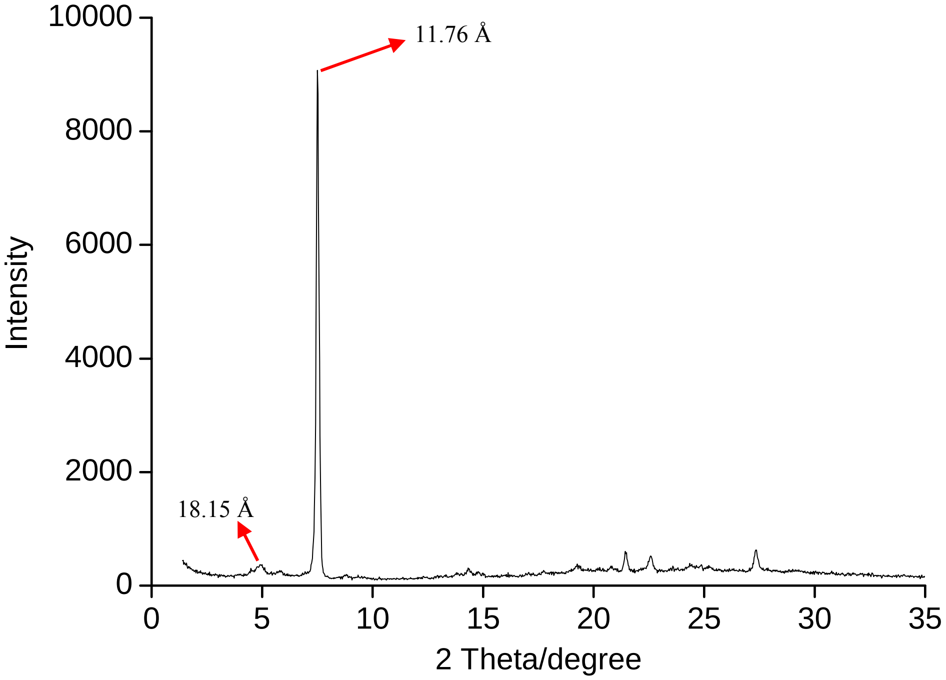

Figure S2. XRD pattern of nanoplates formed by **3** in DMSO/dixoane.

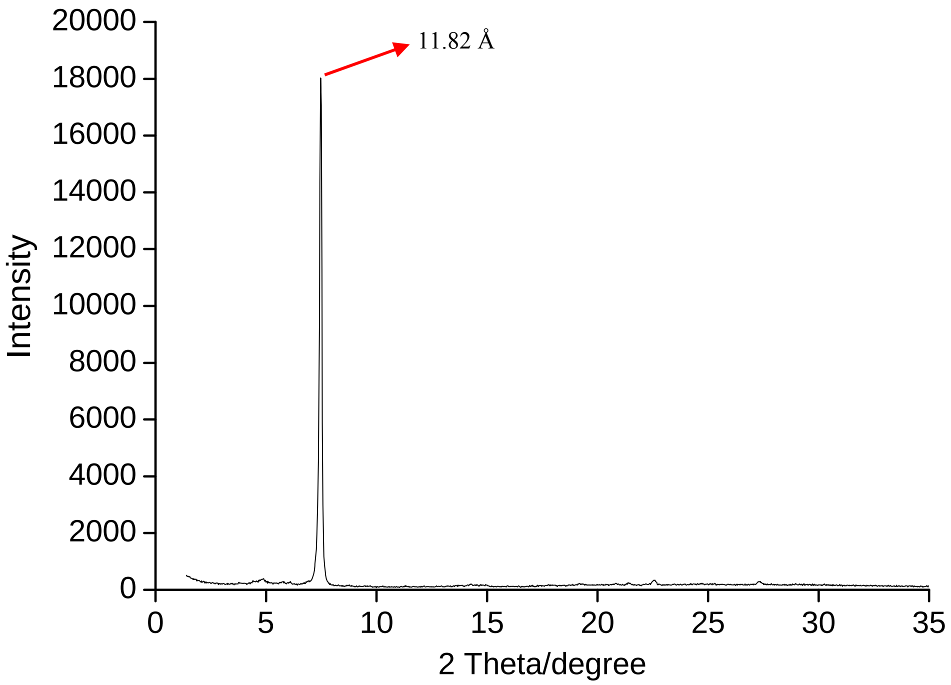

Figure S3. XRD pattern of nanoplates formed by **3** in DMSO/ethyl acetate.

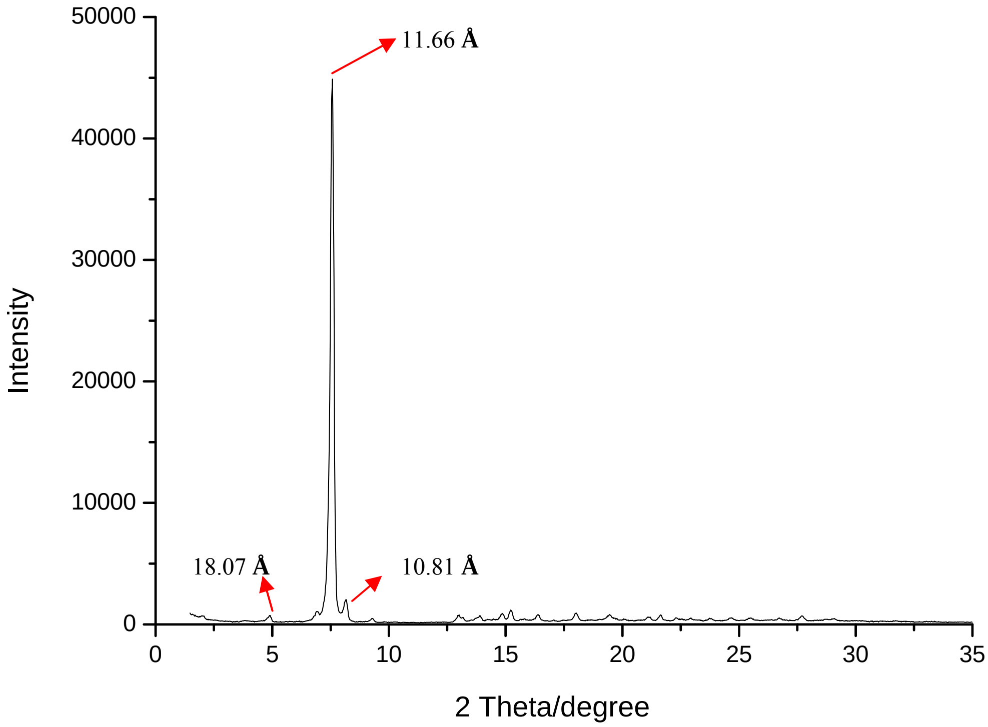

Figure S4. XRD pattern of nanoplates formed by **3** in DMSO/ether.

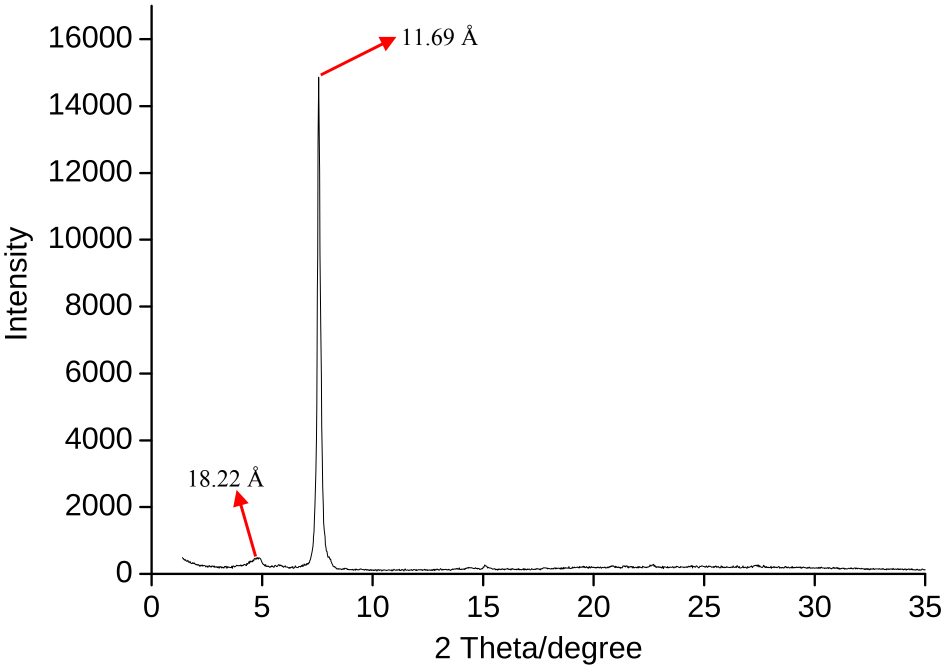

Figure S5. XRD pattern of nanoplates formed by **3** in DMSO/tetrahydrofuran.

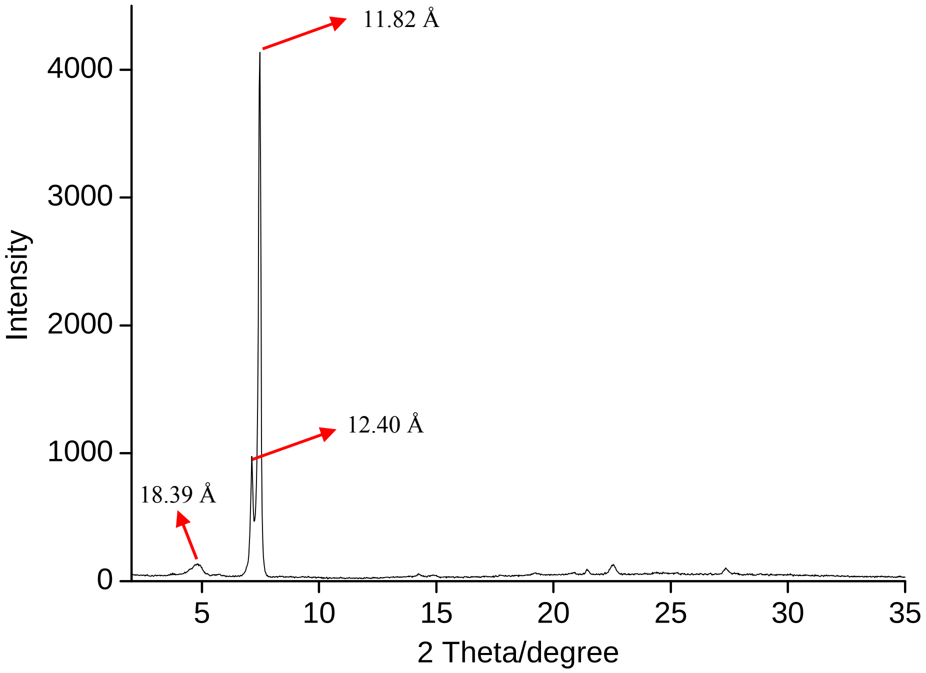

Figure S6. XRD pattern of nanoplates formed by **3** in DMSO/acetone.

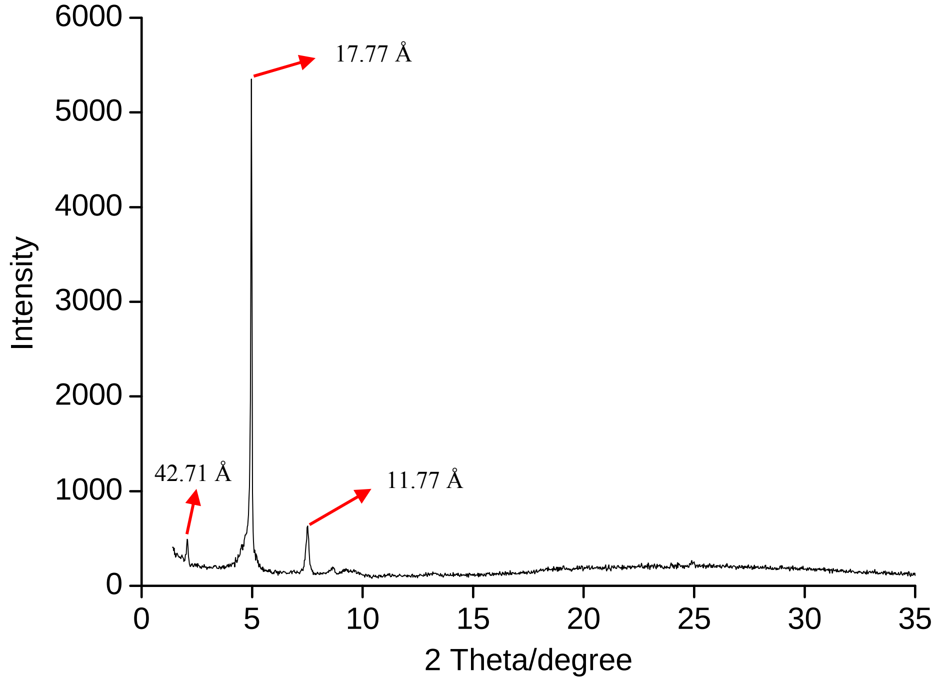

Figure S7. XRD pattern of nanoplates formed by **3** in DMSO/acetonitrile.

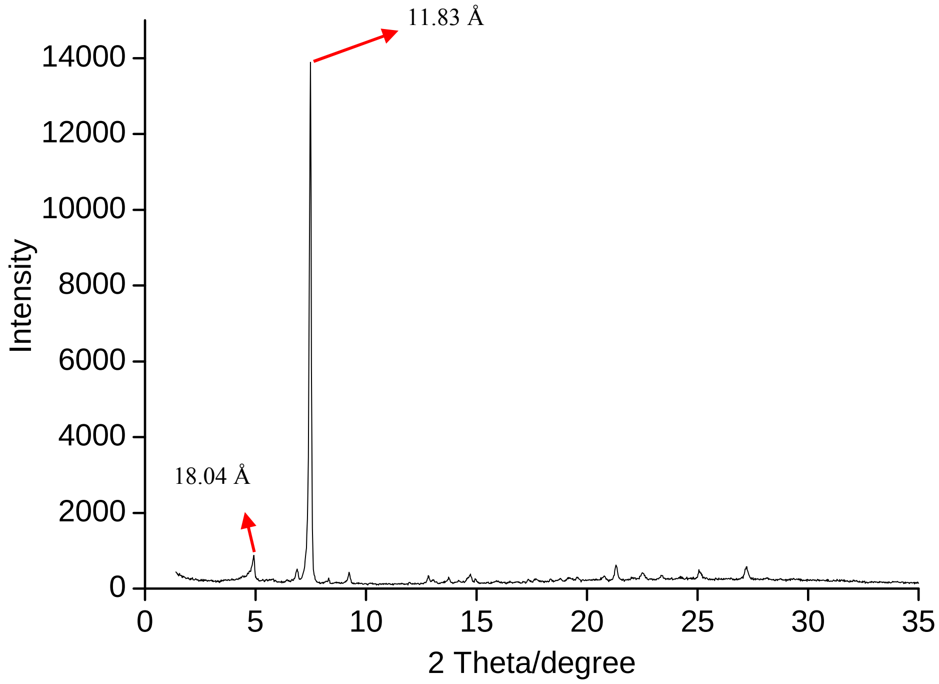

Figure S8. XRD pattern of nanoplates formed by **3** in DMSO/EtOH