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Discrimination of Dicarboxylic Acids via Assembly-Induced Emission

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Supporting Information

General Methods and Materials

The emission spectra were measured using a PerkinElmer LS 55 Fluorescence spectrometer. The absorption spectra were recorded using a Cary 50 Scan UV-Visible spectrophotometer. The ^{1}H and ^{19}F NMR spectra, and the diffusion coefficient measurements were recorded on JEOL ECA-600 and ECA-500 spectrometers, with working frequencies of 600 and 500 MHz, respectively (for ^{1}H nuclei), and using the peaks of residual solvent as standards. Calculations of possible complex geometries were carried out at the B3LYP-D3/6-31G(d) level of theory as implemented in the Gaussian 16 program package.

The following starting materials and solvents were obtained from the commercial sources given in parentheses and used without further purification: spectrophotometric grade *N*,*N*-dimethylformamide (DMF), phthalic acid, isophthalic acid, terephthalic acid, benzoic acid, maleic acid, fumaric acid, malonic acid, formic acid, and butyric acid (Alfa Aesar); oxalic acid (GFS); succinic acid (J. T. Baker); acetic acid (Macron); propionic acid (Fisher). Compound **1** was prepared as previously reported.[1]

Experiments are presented in the order following the discussion of the manuscript.
Compound numbers are identical to those in the main text of the manuscript.

Emission and Absorption Spectra

The crystals of **1** were dissolved in DMF with heating, to prepare a 77.4 μM stock solution. The tested dicarboxylic and monocarboxylic acids were dissolved in DMF and prepared as 550 μM stock solutions. Then, 388 μL of the stock solution of **1** was mixed with 0, 1, 2, 3, 6, 12, 24, or 48 eq of the tested carboxylic acid, and diluted with DMF to 3 mL. The mixture was vigorously stirred for 1 min to yield a final solution with the concentration of **1** being 10 μM. The obtained samples were used to test the emision and absorption spectra.

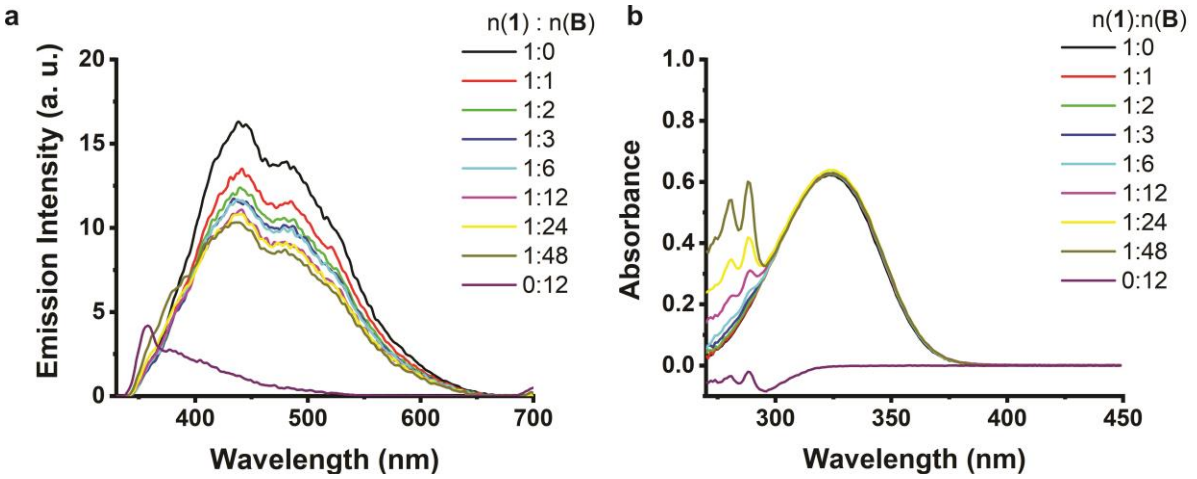

Figure S1. Emission (**a**, λ_{exc} = 320 nm) and adsorption (**b**) spectra of **1** (10 μM, 1 eq) with different eq of **B** in DMF solution.

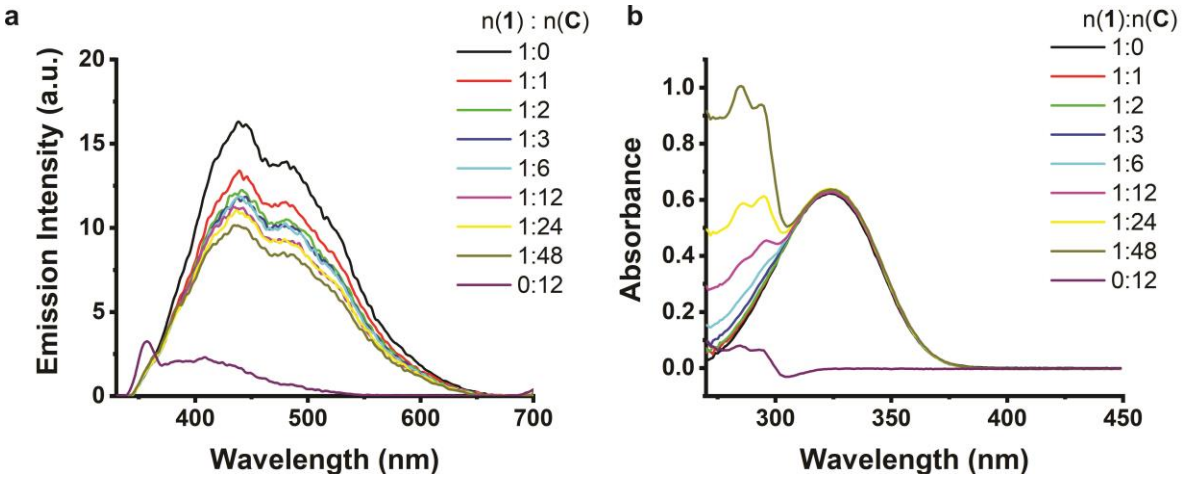

Figure S2. Emission (**a**, λ_{exc} = 320 nm) and adsorption (**b**) spectra of **1** (10 μM, 1 eq) with different eq of **C** in DMF solution.

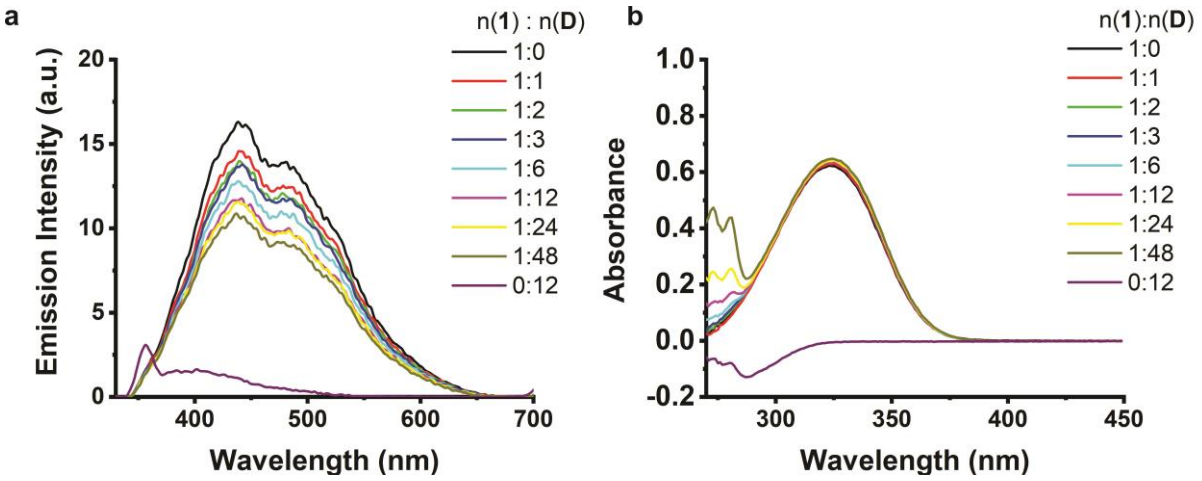

Figure S3. Emission (**a**, λ_{exc} = 320 nm) and adsorption (**b**) spectra of **1** (10 μM, 1 eq) with different eq of **D** in DMF solution.

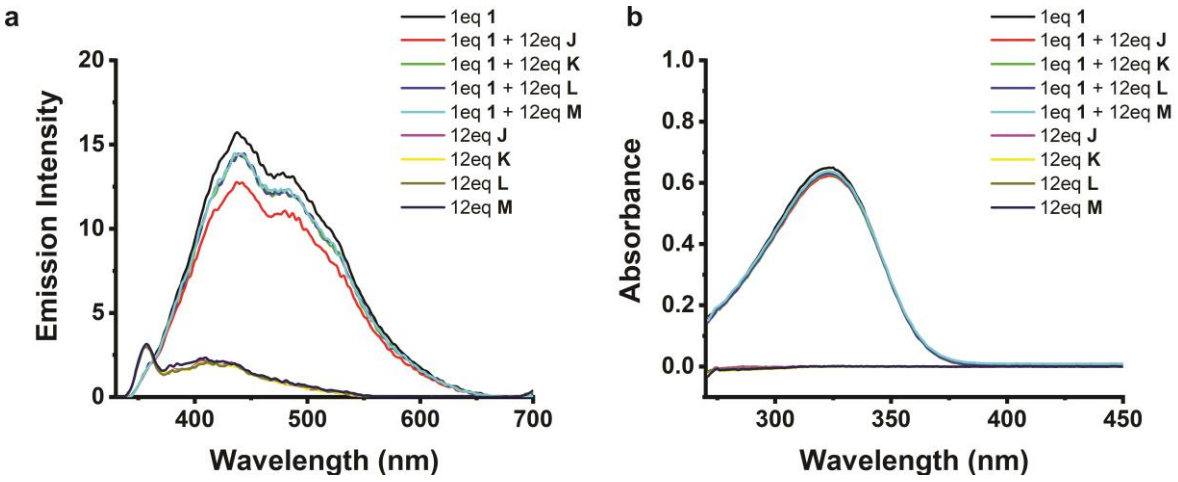

Figure S4. Emission (**a**, λ_{exc} = 320 nm) and absorption (**b**) spectra of **1**(10 μM, 1 eq) with 12 eq of aliphatic monocarboxylic acids **J**, **K**, **L**, and **M**.

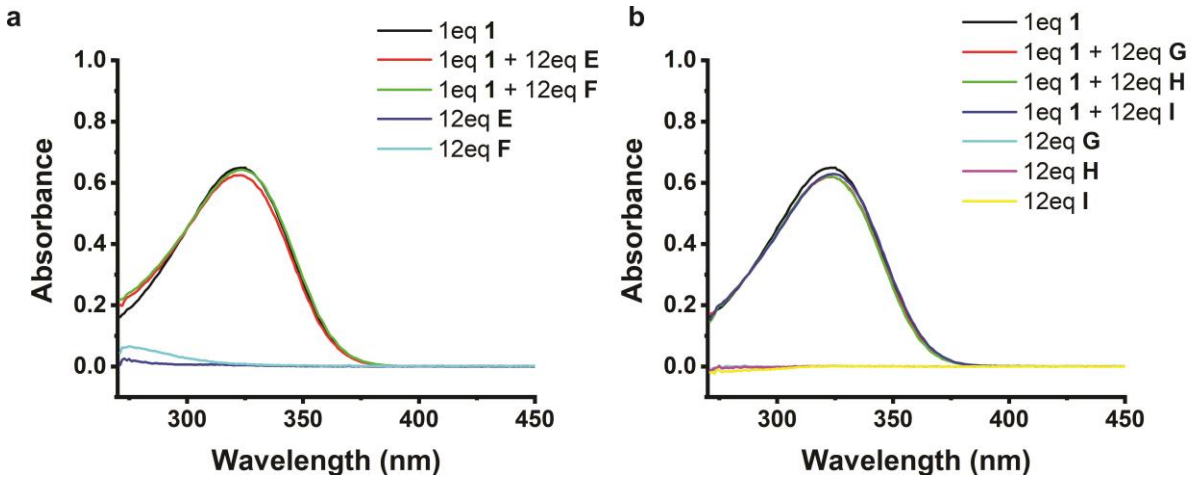

Figure S5. Absorption spectra of **1** (10 μM, 1 eq) with 12 eq of isomers **E** and **F** (**a**) and 12 eq of aliphatic α,ω-diacids **G**, **H**, and **I** (**b**).

Table S1. The data of emission and absorption spectra of the DMF solution of **1** (10 mM, 1 eq) mixed with different aromatic acids (pK_a).[a]

Acid(eq)	**A** (pK_{a1} = 2.9, pK_{a2} = 5.4)[2]			**B** (pK_{a1} = 3.7, pK_{a2} = 4.6)[2]			**C** (pK_{a1} = 3.5, pK_{a2} = 4.3)[2]			**D** (pK_a = 4.2)[2]		
	λ_{ems} (nm)	λ_{abs} (nm)	I/I_0	λ_{ems} (nm)	λ_{abs} (nm)	I/I_0	λ_{ems} (nm)	λ_{abs} (nm)	I/I_0	λ_{ems} (nm)	λ_{abs} (nm)	I/I_0
0	439	323	1.00	439	323	1.00	439	323	1.00	439	323	1.00
1	440	323	0.82	442	325	0.84	439	325	0.83	439	325	0.90
2	440	324	0.71	440	325	0.77	442	323	0.77	440	325	0.86
3	438	324	0.68	434	325	0.74	445	325	0.74	443	324	0.85
6	489	324	1.63	438	324	0.74	440	324	0.74	439	323	0.79
12	490	324	4.40	441	323	0.69	434	324	0.70	442	325	0.73
24	490	323	3.39	441	325	0.69	437	324	0.69	438	325	0.72
48	484	323	1.50	439	324	0.68	435	324	0.65	437	324	0.68

[a] λ_{abs} is the wavelength with local maximum around 323 nm for absorption spectra.

NMR Titrations

The solutions of dicarboxylic acids in DMSO-d_6 were prepared as 86 mM and 432 mM for the titration. Compound **1** (8.6×10^{-4} mmol, 1 eq) was dissolved in 0.5 mL of DMSO-d_6 and titrated with 0, 0.2, 0.4, 0.6, 0.8, 1, 2, 3, 6, 12, 24, and 48 eq of dicarboxylic acids under vigorous stirring and tested by ^{1}H and ^{19}F NMR spectroscopy.

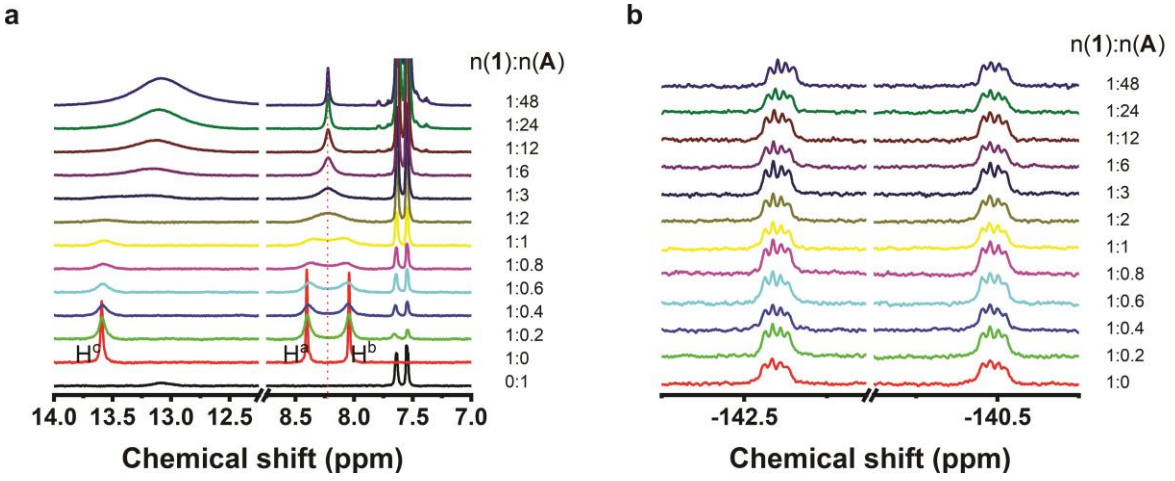

Figure S6. The ^{1}H (**a**) and ^{19}F (**b**) NMR spectra of **1** (1 eq, 8.6×10^{-4} mmol) in 0.5 mL DMSO-d_6 titrated with **A**.

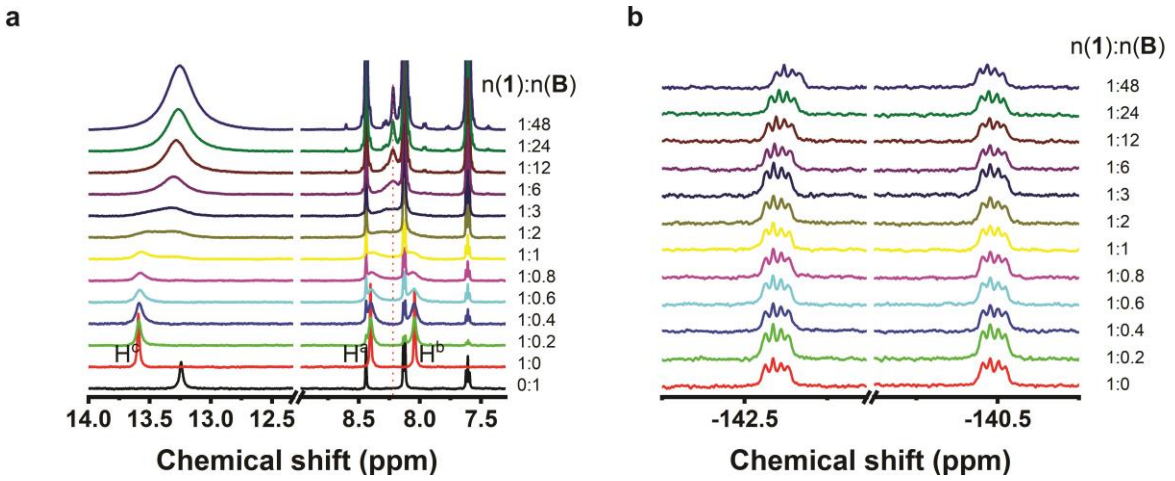

Figure S7. The ^{1}H (**a**) and ^{19}F (**b**) NMR spectra of **1** (1 eq, 8.6×10^{-4} mmol) in 0.5 mL DMSO-d_6 titrated with **B**.

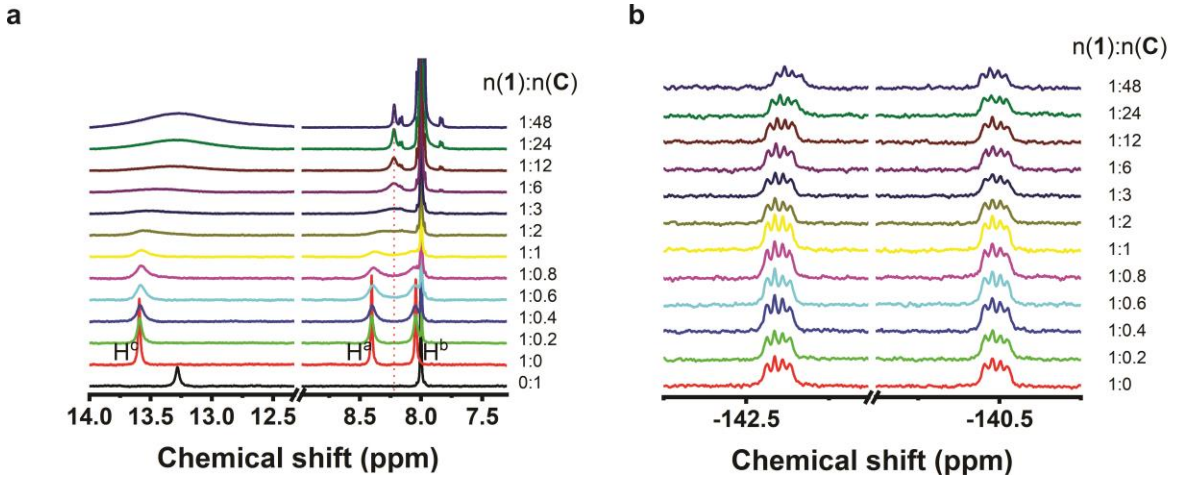

Figure S8. The ^{1}H (**a**) and ^{19}F (**b**) NMR spectra of **1** (1 eq, 8.6×10^{-4} mmol) in 0.5 mL DMSO-d_6 titrated with **C**.

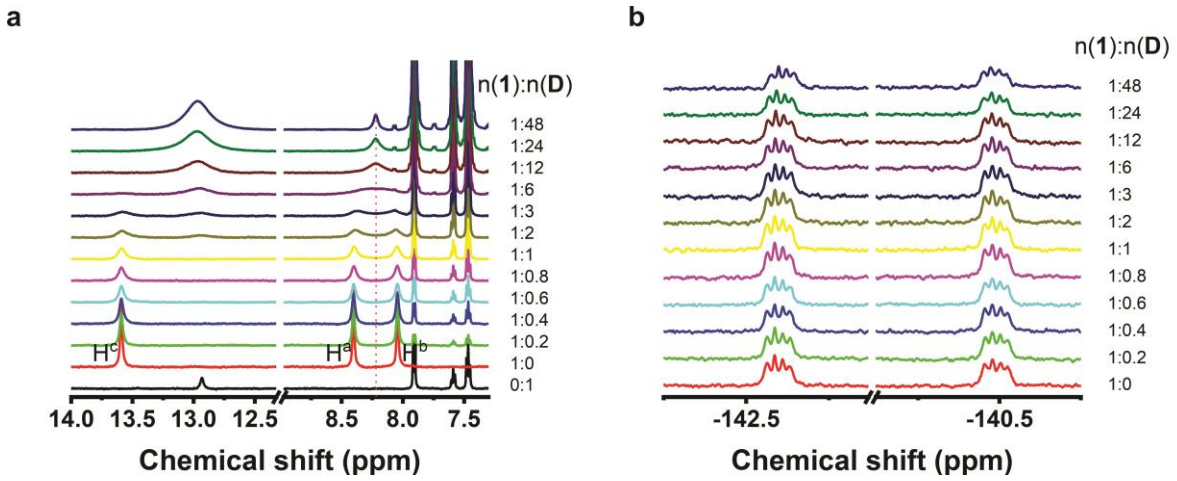

Figure S9. The ^{1}H (**a**) and ^{19}F (**b**) NMR spectra of **1** (1 eq, 8.6×10^{-4} mmol) in 0.5 mL DMSO-d_6 titrated with **D**.

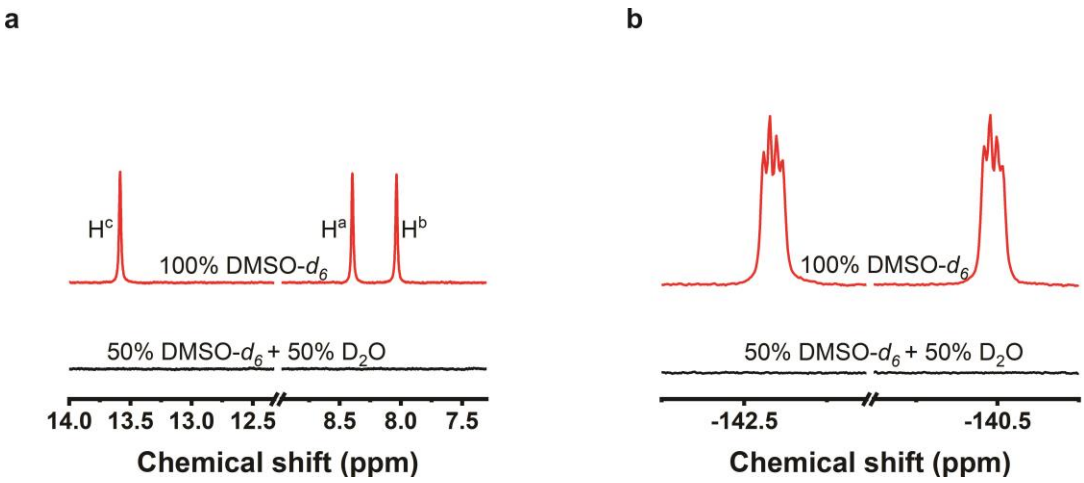

Figure S10. The ^{1}H (**a**) and ^{19}F (**b**) NMR spectra of **1** (1 eq, 6.9×10^{-4} mmol) in DMSO-d_6 and a 50:50 (v:v) mixture of DMSO-d_6 and D_2O.

Models for *D(calc)*

The theoretical value of the diffusion coefficient, *D(calc)*, can be obtained with suitable geometric model by a modified Stokes-Einstein equation; see equations (1)–(4) below. The theoretical diffusion coefficients of compounds with three branches and similar geometries to **1**, were evaluated successfully.[3] The *D(calc)* for **1** and possible complexes formed by **1** and **A** were calculated based on oblate or cylinder models (Figure S11). The geometric parameters *a* and *b* for oblate model or *L* and *d* for the oblate model and the *D(calc)* were shown in Figure S12.

According to reference 3, the η in equation (1) was calculated as 0.0022 Pa s at T = 292.55 K (test temperature), and the van der waals radius of DMSO, $r_{wdw,}$ is 2.541 Å.

$$D = \frac{k_B T}{c f_s \pi \eta r_h} \qquad (1)$$

$$c = \frac{6}{1+0.695(\frac{r_{vdw}}{r_h})^{2.234}} \qquad (2)$$

$$f_s = \frac{\sqrt{\frac{b^2}{a}-1}}{(\frac{b}{a})^{\frac{2}{3}}\tan^{-1}\sqrt{\frac{b^2}{a}-1}}, or\ f_s =$$

$$1.0304 + 0.0193\left[\ln\left(\frac{L}{d}\right)\right] + 0.06229[\ln(\frac{L}{d})]^2 + 0.00476[\ln(\frac{L}{d})]^3 + 0.00166[\ln(\frac{L}{d})]^4 + 2.66 \times 10^{-6}[\ln(\frac{L}{d})]^7 \qquad (3)$$

$$r_h = \sqrt[3]{ab^2} or \sqrt[3]{\frac{3d^2L}{16}} \qquad (4)$$

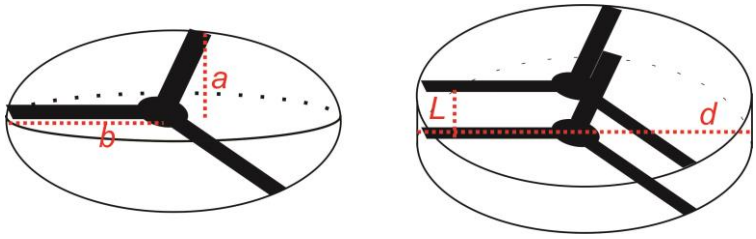

Figure S11. Oblate (left) and cylinder (right) models and the corresponding geometric parameters.

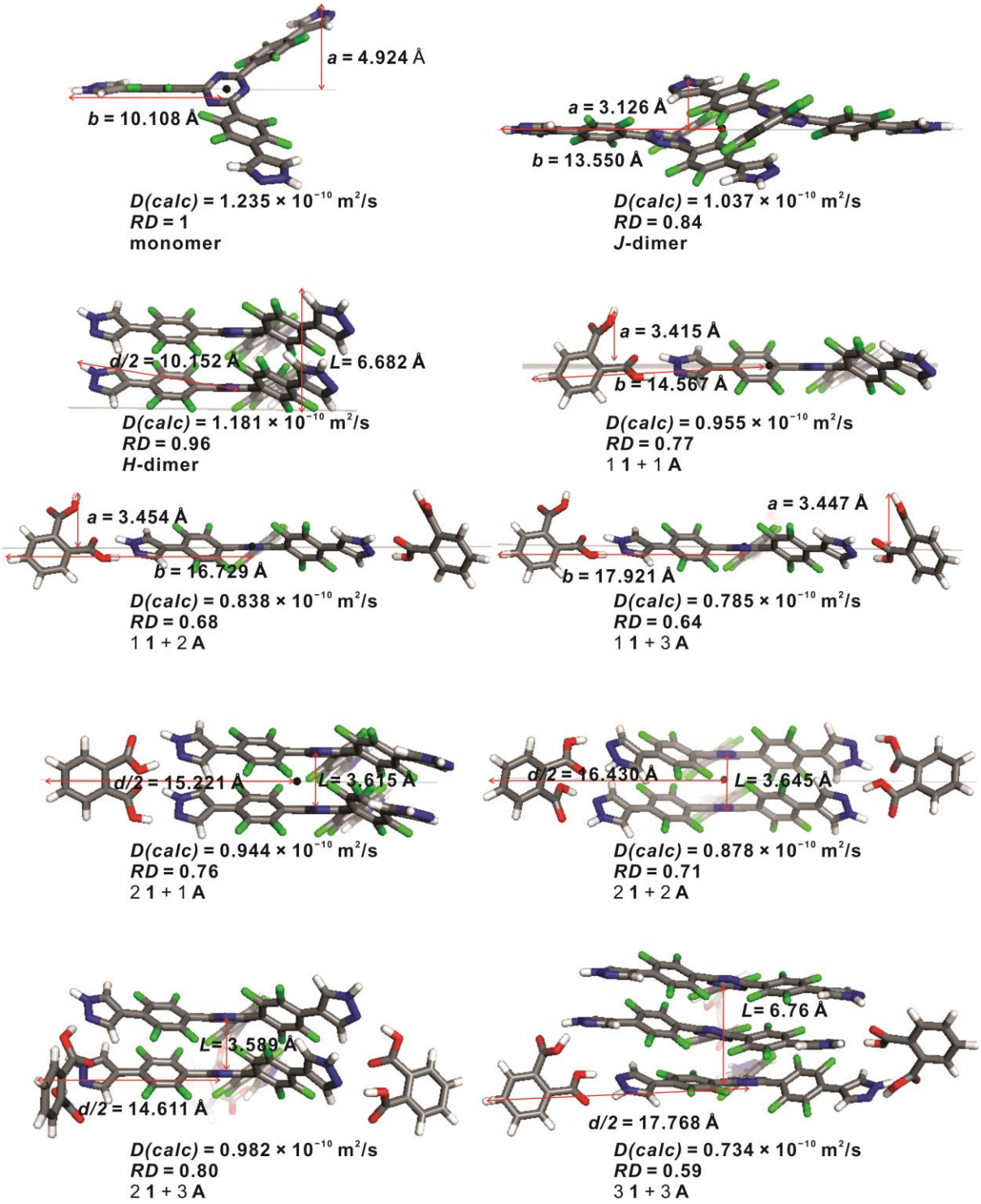

Figure S12. Possible structures of complexes formed between **1** and **A**, their *D(calc)* values, and relative diffusion coefficients (*RD*). The structures of the monomer and the *J*-dimer were obtained from the crystal structure of **1**.[1] The rest of these models were optimized at the B3LYP-D3/6-

31G(d) level of theory by Gaussian 16.[4] Element colors: H—white, N—blue, C—gray, F—green, O—red. Centroid of a complex is represented as a black sphere dot.

Diffusion NMR Spectrum Measurements

A 2.1M solution of compound **A** in DMSO-d_6 was prepared for the titration. The tested samples were prepared by dissolving **1** (6.9×10^{-4} mmol, 1 eq) in 0.5 mL of DMSO-d_6, and titrating the resulting solution with 0, 12, 18, 24, and 48 eq of **A** under vigorous stirring. The diffusion NMR spectrum measurements were carried out based on the ^{19}F NMR signal (564.73 MHz) with a bipolar pulse pair longitudinal eddy current delay (BPP-LED) sequence. The diffusion time and delta values were set as 0.2 s and 4.5 ms, respectively. The pulsed-field gradient was linearly increased from 20 to 275 mT/m in 8 steps. The temperature during test was 292.55 ± 0.2 K. Each sample was tested three times under the same conditions. The diffusion-ordered NMR spectroscopy (DOSY) data were obtained after processing the data using Delta™ NMR Data Processing Software.

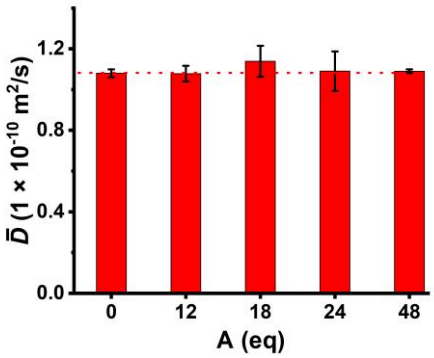

Figure S13. The average diffusion coefficient ($\overline{D}$) at −140.507 ppm of ^{19}F NMR of **1** (1 eq, 6.9×10^{-4} mmol) in 0.5mL of DMSO-d_6 mixed with different eq **A**.

As shown in Figure S13 and Table S2, the mean values of three test for $\overline{D}$ at −140.507 ppm were 1.080, 1.078, 1.139, 1.091, 1.090×10^{-10} m^2 s^{-1} as 1 eq of **1** was mixed with 0, 12, 18, 24, and 48 eq **A**, respectively. Roughly estimated by the inverse proportional relation to D, the hydrodynamic radius of the solute was changed as 0.2%, −5.2%, −1.0%, and −0.9% after the titration of 12, 18, 24, and 48 eq of **A**, respectively. This result shows that no aggregation occurred.

The diffusion data were processed by DOSY analysis as shown in Table S3. Possible structures were listed and compared with the corresponding *D(calc)* in Figure S12. For the solution of **1** in DMSO-d_6 solution, the monomer, and *J*- and *H*-dimers were detected. The addition of **A** into the solution of **1** in DMSO-d_6 caused the formation of complexes described as "1 molecule of **1** with 1 or 2 molecules of **A**" and "2 molecules of **1** with 1, 2, or 3 molecules of **A**". The repeatability of DOSY

analysis was poor, because the ^{19}F NMR signals from all species overlapped. However, despite this issue, the DOSY data excluded the presence of larger assemblies, such as those denoted "3 **1** + 3 **A**", also supporting the notion that no aggregation occurred. Therefore, the turn ON of the fluorescence of **1** by the addition of **A** was not due to aggregation.

Note: To obtain good NMR response signals, the NMR tests were carried out at much higher concentration, about 1.38×10^{3} μM, than the emission and absorption spectra tests (10 μM). The higher concentration is not suitable for emission and absorption spectra tests, because the absorbance exceeds the instrument test limits and the solutions stopped being fluorescent under such high concentration. However, the diffusion NMR spectrum measurements and DOSY analysis can still provide the information of the solute's size and possible structures of the complexes formed by **1** and **A**.

Table S2. The average diffusion coefficient ($\overline{D}$) at each peak of ^{19}F NMR of **1** (1 eq, 6.9×10^{-4} mmol) in 0.5 mL of DMSO-d_6 mixed with different eq of **A**.

Sample	Test#	Peak(ppm)	$\overline{D}$ (1×10^{-10} m^2/s)	Peak(ppm)	$\overline{D}$ (1×10^{-10} m^2/s)
1 eq **1**	1	−140.507	1.058	−142.403	1.159
		−140.528	1.096	−142.421	1.152
	2	−140.507	1.088	−142.403	1.077
		−140.528	1.128	−142.421	1.076
				−142.440	1.120
	3	−140.507	1.095	−142.403	1.153
		−140.528	1.137	−142.421	1.154
		−140.547	1.182		
1 eq **1** + 12 eq **A**	1	−140.507	1.121	−142.397	1.214
		−140.525	1.209	−142.418	1.258
	2	−140.507	1.045	−142.397	1.078
		−140.525	1.096	−142.418	1.037
				−142.434	1.137
	3	−140.507	1.070	−142.397	1.057
		−140.525	1.071	−142.418	1.087
1 eq **1** + 18 eq **A**	1	−140.507	1.227	−142.397	1.265
		−140.525	1.199	−142.418	1.258
		−140.544	1.161	−142.434	1.226
	2	−140.489	1.187	−142.394	1.116
		−140.507	1.101	−142.415	1.14
		−140.525	1.067	−142.434	1.128
	3	−140.507	1.090	−142.397	1.212
		−140.525	1.194	−142.415	1.071
				−142.434	1.003
1 eq **1** + 24 eq **A**	1	−140.507	1.121	−142.394	1.165

			−140.528	1.177	−142.415	1.103
	2		−140.507	1.169	−142.394	1.031
			−140.528	1.130	−142.410	1.058
	3		−140.507	0.982	−142.394	1.000
			−140.528	1.113	−142.415	1.204
1 eq **1** + 48 eq **A**	1		−140.507	1.094	−142.373	1.075
			−140.528	1.115	−142.391	1.047
			−140.547	1.068	−142.409	1.043
					−142.428	1.093
	2		−140.507	1.097	−142.391	1.145
			−140.528	1.065	−142.409	1.076
			−140.547	1.080	−142.428	1.060
	3		−140.507	1.080	−142.391	1.106
			−140.528	1.094	−142.409	1.054
			−140.547	1.102	−142.428	1.101

Table S3. The DOSY data of **1** (1 eq, 6.9×10^{-4} mmol) in 0.5mL of DMSO-d_6 mixed with 0, 12, 18, 24, 48 eq **A** and possible structure for observed species.

	Test #	Species	D(1×10^{-10} m^2/s) and distrubtion area	*RD* and distribution area[a]	possible structure[b]
1 eq **1**	1	1st	1.104 [1.091,1.118]	0.89 [0.88, 0.91]	***J* or *H*-dimer**
		2nd	1.275 [1.272,1.279]	1.03 [1.03, 1.04]	**monomer or *H*-dimer**
	2	1st	1.054 [1.034,1.072]	0.85 [0.84, 0.87]	***J*-dimer**
		2nd	1.114 [1.109,1.124]	0.90 [0.90, 0.91]	***H*-dimer**
		3rd	1.168 [1.157,1.179]	0.95 [0.94, 0.95]	**monomer or *H*-dimer**
	3	1st	1.108 [1.093,1.110]	0.90 [0.89, 0.90]	***J*-dimer**
		2nd	1.225 [1.216,1.234]	0.99 [0.98, 1.00]	**monomer or *H*-dimer**
1 eq **1** + 12 eq **A**	1	1st	0.942 [0.905, 0.978]	0.76 [0.73, 0.79]	protonated ***J*-dimer**[c] 1 **1** + 1 **A** 1 **1** + 2 **A** 2 **1** + 1 **A** 2 **1** + 2 **A** 2 **1** + 3 **A**
		2nd	1.188 [1.159, 1.189]	0.96 [0.94, 0.96]	protonated **monomer or *H*-dimer**[c]
	2	1st	1.100 [1.087, 1.103]	0.89 [0.88, 0.89]	protonated ***J*-dimer**[c]
		2nd	1.176 [1.164, 1.180]	0.95 [0.94, 0.96]	protonated **monomer or *H*-dimer**[c]
	3	1st	1.123 [1.110,1.135]	0.91 [0.90,0.92]	protonated ***H*-dimer**[c]

1 eq **1** + 18 eq **A**	1	1st	0.960 [0.895,1.025]	0.78 [0.72,0.83]	protonated ***J*-dimer**[c] 1 **1** + 1 **A** 1 **1** + 2 **A** 2 **1** + 1 **A** 2 **1** + 2 **A** 2 **1** + 3 **A**
		2nd	1.205 [1.169,1.215]	0.98 [0.95, 0.98]	protonated **monomer or *H*-dimer**[c]
		3rd	1.543 [1.497,1.591]	1.25 [1.21,1.29]	?[d]
	2	1st	1.121 [1.099,1.126]	0.91 [0.89,0.91]	protonated ***J* or *H*-dimer**[c]
		2nd	1.393 [1.345,1.440]	1.13 [1.09,1.17]	?[b]
	3	1st	1.119 [1.103,1.137]	0.91 [0.89,0.92]	protonated ***J* or *H*-dimer**[c]
		2nd	1.352 [1.332,1.374]	1.09 [1.08,1.11]	?[d]
1 eq **1** + 24 eq **A**	1	1st	1.118 [1.096,1.133]	0.91 [0.89,0.92]	protonated ***J* or *H*-dimer**[c]
		2nd	1.444 [1.366,1.524]	1.17 [1.11,1.23]	?[d]
	2	1st	0.971 [0.957,0.986]	0.79 [0.77,0.80]	protonated ***J*-dimer**[c] 1 **1** + 1 **A** 2 **1** + 1 **A** 2 **1** + 3 **A**
		2nd	1.064 [1.049,1.076]	0.86 [0.85,0.87]	protonated ***J*-dimer**[c] 2 **1** + 3 **A**
		3rd	1.118 [1.107,1.122]	0.90 [0.90,0.91]	protonated ***H*-dimer**[c]
	3	1st	1.017 [0.998,1.036]	0.82 [0.81,0.84]	protonated ***J*-dimer**[c] 1 **1** + 1 **A** 2 **1** + 1 **A** 2 **1** + 3 **A**
		2nd	1.116 [1.104,1.121]	0.90 [0.89,0.91]	protonated ***J* or *H*-dimer**[c]
1 eq **1** + 48 eq **A**	1	1st	1.059 [1.042,1.061]	0.86 [0.84,0.86]	protonated ***J*-dimer**[c] 2 **1** + 3 **A**
		2nd	1.108 [1.095,1.111]	0.90 [0.89,0.90]	protonated ***J*-dimer**[c]
		3rd	1.255 [1.205,1.306]	1.02[0.98, 1.06]	protonated **monomer or *H*-dimer**[c]
	2	1st	1.021 [1.006,1.027]	0.83 [0.81,0.84]	protonated ***J*-dimer**[c] 1 **1** + 1 **A** 2 **1** + 1 **A** 2 **1** + 3 **A**
		2nd	1.106 [1.102,1.118]	0.90 [0.89,0.91]	protonated ***J*-dimer**[c]
	3	1st	0.982 [0.949,1.018]	0.80 [0.77,0.82]	protonated ***J*-dimer**[c] 1 **1** + 1 **A** 2 **1** + 1 **A** 2 **1** + 3 **A**
		2nd	1.102 [1.083,1.112]	0.89 [0.88,0.90]	protonated ***J*-dimer**[c]

3rd	1.365 [1.361,1.367]	1.11 [1.10,1.11]	?[d]

[a] Relative diffusion coefficient (*RD*) was the value relative to the *D(calc)* value of monomer.

[b] The error of the judgement: the difference of the *RD* values between a tested value and a model's value (Figure S12) < 0.05.

[c] The monomer or dimer detected in acidic environment was assumed to be protonated based on the ^{1}H NMR titration.

[d] The value that is bigger than the monomer, which is abnormal.

Models for *cis*- and *trans*-Ethylenedicarboxylic Acids Interacting with 1

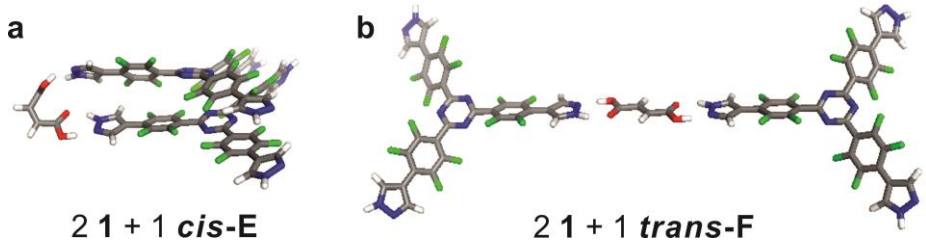

Figure S14. The optimized structures of one molecule of either the *cis*- (**a**) or *trans*- (**b**) ethylenedicarboxylic acid interacting with two molecules of **1**. These models were optimized at the B3LYP-D3/6-31G(d) level of theory, using Gaussian 16.[4]

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