

The first X-Ray crystallographic evidence of a cyclic aniline trimer via self-complementary NH- π interactions: The aniline inclusion both inside and outside the macrocyclic cavity

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1. General experimental methods and experimental procedures for 2 and 3

IR spectra were recorded on a JASCO FT/IR-470 plus Fourier Transform Infrared Spectrometer and measured as KBr pellets. ^1H NMR spectra were determined in CDCl_3 or $\text{DMSO-}d_6$ with a JEOL JNM-AL 300 spectrometer. Chemical shifts (δ) are given as δ values (ppm) relative to tetramethylsilane (TMS). The coupling constants (J) are given in hertz. Elemental analyses were performed by the Service Centre of the Elemental Analysis of Organic Compound affiliates with the Faculty of Science, Kyushu University. FAB-MS spectra were recorded with a JEOL JMS-SX/SX 102A mass spectrometer with *m*-nitrobenzyl alcohol as a matrix. ESI-MS spectra were recorded with a JEOL JMS-T100CS mass spectrometer. UV/Vis spectra were measured on a JASCO V-570 spectrophotometer in a 1 cm width quartz cell. Analytical TLC was carried out on silica gel Merck 60 F₂₅₄. Column chromatography was carried out on silica gel (KANTO 60N). THF was distilled from sodium and benzophenone under an argon atmosphere just before use. Aniline was distilled from Zn powder just before use.

Pyromellitic Diimide-Based Macrocycles 2 and 3. A solution of 2,7-bis(aminomethyl)-3,6-di-*n*-hexyloxynaphthalene (1.06 g, 2.74 mmol) in dry THF (100 mL) and a solution of pyromellitic dianhydride (968 mg, 2.74 mmol) in dry THF (100 mL) were simultaneously added to dry THF (50 mL) at 50 °C over a period of 4 h with stirring under an argon atmosphere. After the addition, the reaction mixture was stirred at 50 °C for 24 h, and the reaction mixture was evaporated in vacuo to dryness to give the amic acid. In the ^1H NMR spectra, the broad COOH signals of the intermediate amic acid derivatives were observed at around 13–14 ppm in $\text{DMSO-}d_6$ solution. A solution of the amic acid and NaOAc (985 mg, 11.9 mmol) in Ac_2O (48 mL) were stirred at room temperature for 3 h under an argon atmosphere, and then heated at 100 °C for 2 h. The reaction mixture was poured into water (300 mL), and the precipitate was collected by filtration. The precipitate was continuously extracted with CHCl_3 in a Soxhlet extractor, and the extract was evaporated in vacuo to dryness. The residue was purified by silica gel column chromatography eluting with CHCl_3 to give **2** in 14% yield (217 mg, 0.19 mmol) as pale green powder and **3** in 4% yield (60 mg, 353 μmol) as green powder. A single crystal of **2**·(toluene)₄ was grown by the toluene solution.

2: mp > 300 °C; IR (KBr) ν_{max} 2954, 2929, 2868, 2858, 1776 ($\nu_{\text{C=O}}$), 1728 ($\nu_{\text{C=O}}$), 1639, 1419, 1381, 1319, 1252, 1221, 1140, 1119, 1022 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.93 (t, J = 6.4 Hz, 12 H, CH_3), 1.37–1.42 (m, 16 H, CH_2), 1.52–1.59 (m, 8 H, CH_2), 1.90 (tt, J = 6.4 Hz, 8 H, CH_2), 4.12 (t, J = 6.4 Hz, 8 H, OCH_2), 5.06 (s, 8 H, benzyl H), 6.80 (s, 4 H, ArH), 7.05 (s, 4 H, ArH), 8.42 (s, 4 H, ArH); ^{13}C NMR (75 MHz, CDCl_3) δ 14.1, 22.6, 25.9, 29.2, 31.6, 68.1, 77.2, 105.0, 118.7, 122.3, 122.4, 122.6, 134.5, 137.4, 154.8, 165.8; FAB-MS (NBA,

positive) 1136 (M^+). HR-FAB-MS (NBA, positive) m/z ; calcd. for $C_{68}H_{72}N_4O_{12}$: 1136.5147 (M^+), found: 1136.5164. Anal. Calcd. For $C_{68}H_{72}N_4O_{12} \cdot 0.07CHCl_3$: C, 71.36; H, 6.34; N, 4.89. Found: C, 71.35; H, 6.38; N, 4.90.

3: mp > 300 °C; IR (KBr) ν_{max} 2953, 2929, 2870, 1774 ($\nu_{C=O}$), 1724 ($\nu_{C=O}$), 1637, 1506, 1385, 1346, 1254, 1225, 1111 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, $J = 6.5$ Hz, 18 H, CH_3), 1.31–1.40 (m, 24 H, CH_2), 1.43–1.49 (m, 12 H, CH_2), 1.83 (tt, $J = 6.4$ Hz, 12 H, CH_2), 4.02 (t, $J = 6.4$ Hz, 12 H, OCH_2), 5.02 (s, 12 H, benzyl H), 6.95 (s, 6 H, ArH), 7.46 (s, 6 H, ArH), 8.27 (s, 6 H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 22.6, 25.9, 29.1, 31.6, 68.1, 77.2, 104.8, 118.4, 122.3, 122.6, 128.1, 135.4, 137.3, 155.6, 165.9; FAB-MS (NBA, positive) 1705 [$(M+H)^+$]. HR-FAB-MS (NBA, positive) m/z ; calcd. for $C_{102}H_{108}N_6O_{18}$: 1704.7720 (M^+), found: 1704.7729.

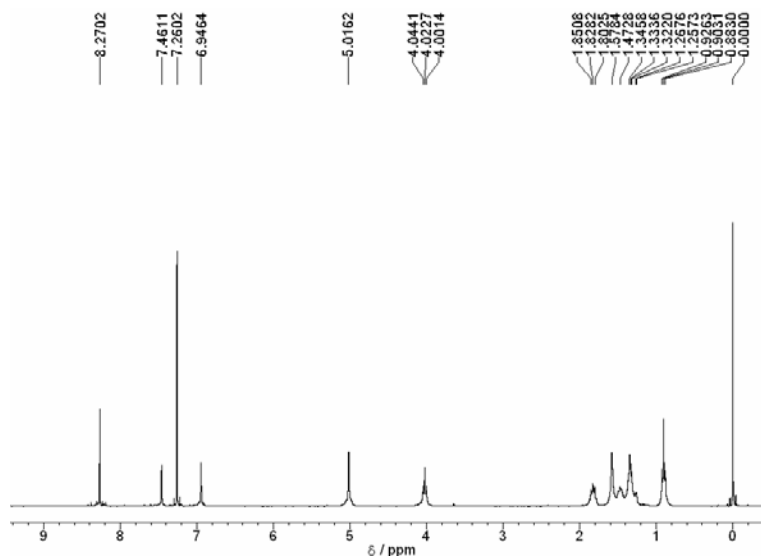


Figure S3. ^1H NMR spectra of [3 + 3] macrocycle **3** in CDCl_3 solution.

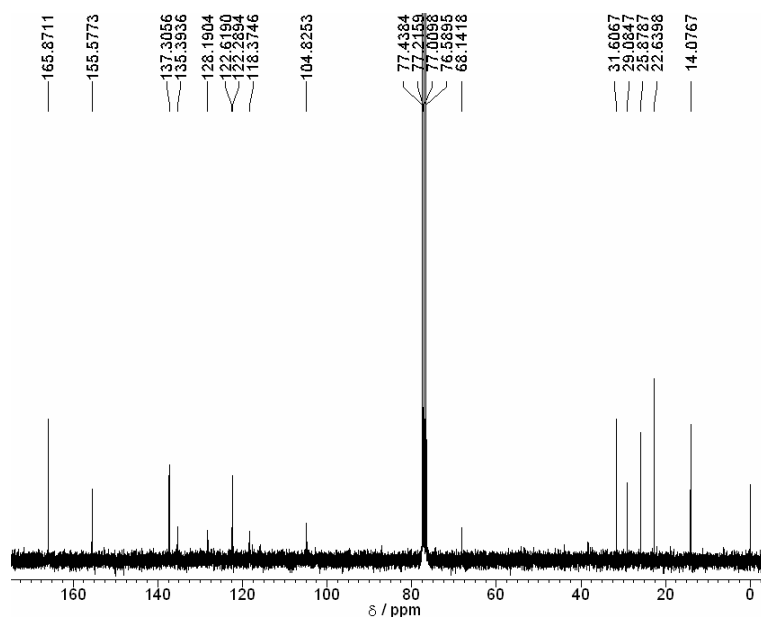


Figure S4. ^{13}C NMR spectra of [3 + 3] macrocycle **3** in CDCl_3 solution.

3.

NOE or ROE spectra of 1-3 in CDCl₃ solution

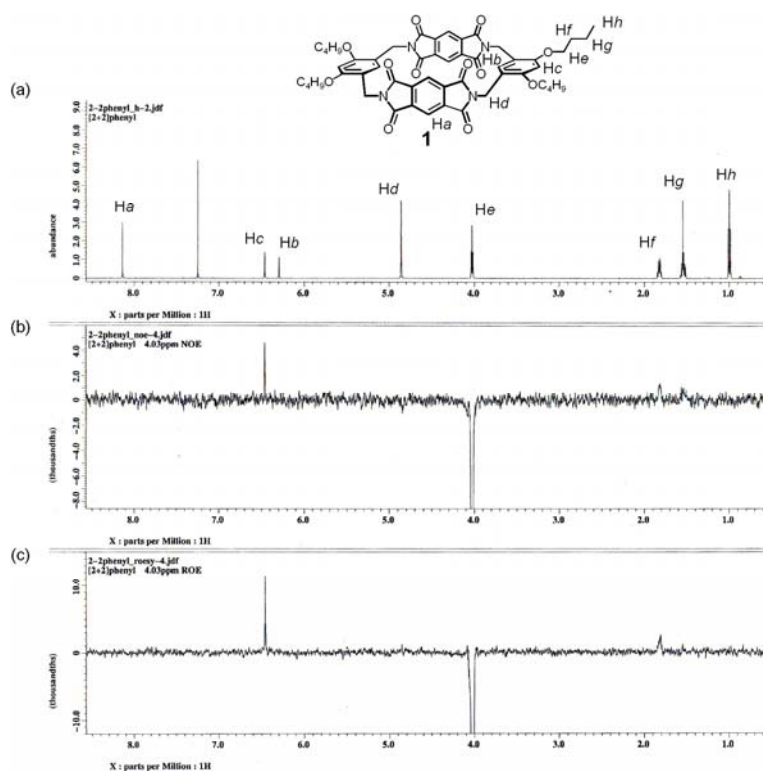


Figure S5. (a) ¹H NMR (b) NOE (c) ROE spectra of **1** in CDCl₃ solution.

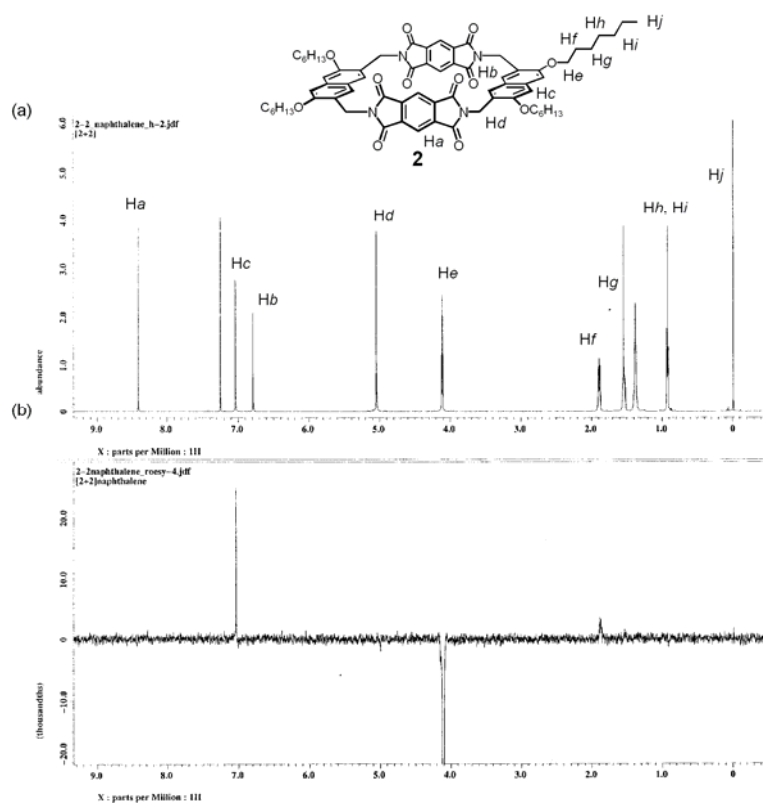


Figure S6. (a) ¹H NMR (b) NOE spectra of **2** in CDCl₃ solution.

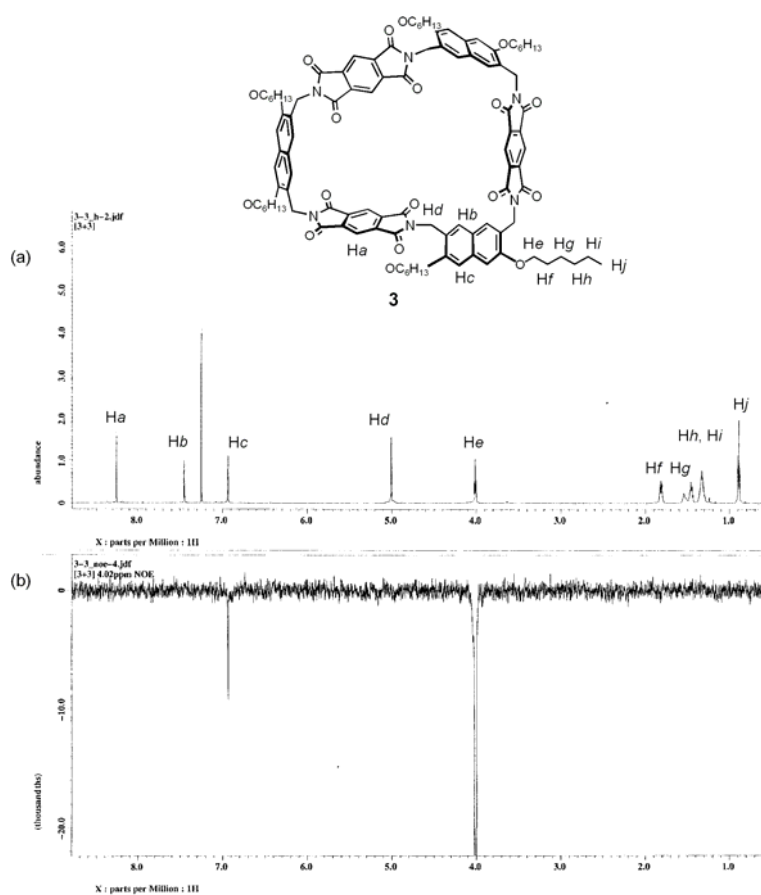


Figure S7. (a) ^1H NMR (b) NOE spectra of **3** in CDCl_3 solution.

4. X-ray Crystallographic Structure Analysis^{S1}

X-ray Crystal Structure Analysis of 2·(toluene)₄. X-ray crystallography was performed on a Rigaku RAXIS RAPID imaging plate diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71069$). The data were collected at 113 K using ω scan in the θ range of 1.1–27.5 deg. A total of 58764 reflections were measured, of which 18092 were independent reflections ($R_{\text{int}} = 0.0840$). The structure was solved by direct methods (Sir97) and refined by the full-matrix least-squares on F^2 (SHELXL-97). All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. One toluene molecule was disordered dynamically and solved using appropriate disorder models. The crystal data are as follows: C₉₆H₁₀₄N₄O₁₂; FW = 1505.83, crystal size 0.55 × 0.51 × 0.12 mm³, Monoclinic, $P2_1/c$, $a = 12.0793(4)$ Å, $b = 29.4107(9)$ Å, $c = 23.5417(8)$ Å, $\beta = 97.9242(9)^\circ$, $V = 8283.6(5)$ Å³, $Z = 4$, $D_c = 1.207$ g cm⁻³. The refinement converged to $R_1 = 0.0655$, $wR_2 = 0.1655$ for $I > 2\sigma(I)$, $R_1 = 0.1187$, $wR_2 = 0.1888$, GOF = 1.087 for all data. CCDC-658507 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Service via www.ccdc.cam.ac.uk/data_request/cif.

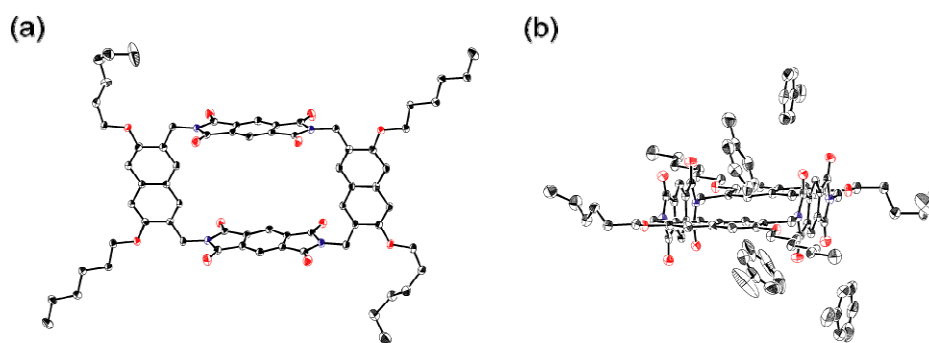


Figure S8. ORTEP drawings of 2·(toluene)₄. The atoms are drawn as 50% probability level of thermal ellipsoids and hydrogen atoms are omitted for clarity. (a) side view, toluene molecules are omitted for clarity; (b) bird's-eye view.

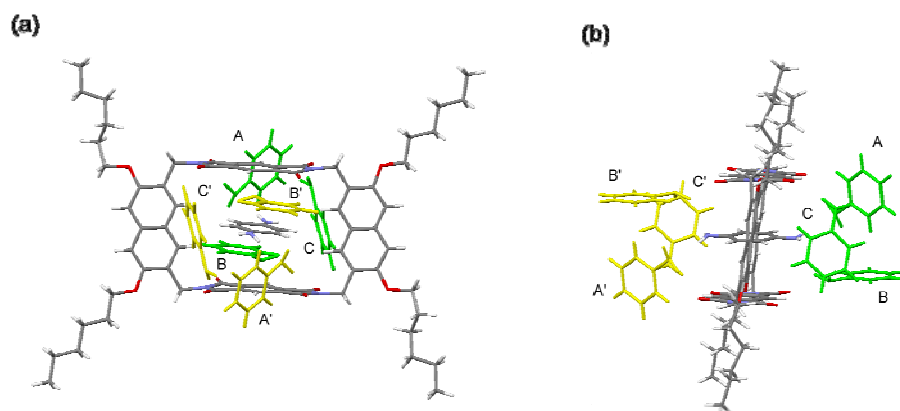


Figure S9. X-ray crystal structure of 2-(aniline)_7 . The two types of cyclic aniline trimers with *R* and *S* configurations are represented by yellow and green colors, respectively.

5. Complexation studies

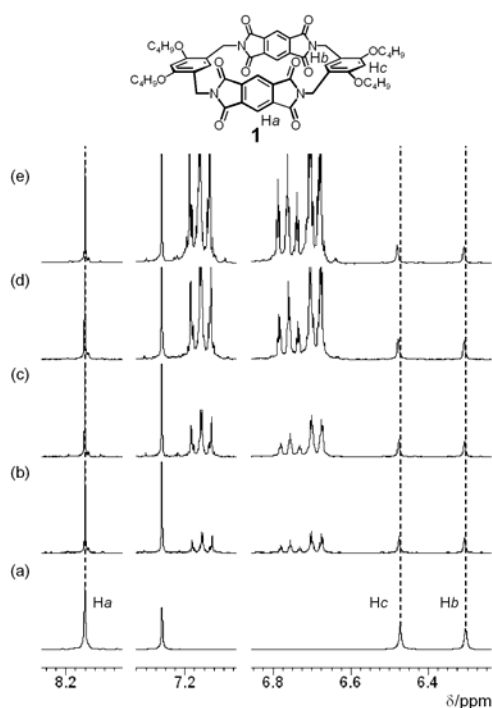


Figure S9. ^1H NMR observation of **1** recorded in CDCl_3 at 5×10^{-3} M (300 MHz, 25 °C) in the presence of (a) 0, (b) 2, (c) 5, (d) 10, or (e) 20 equiv of aniline.

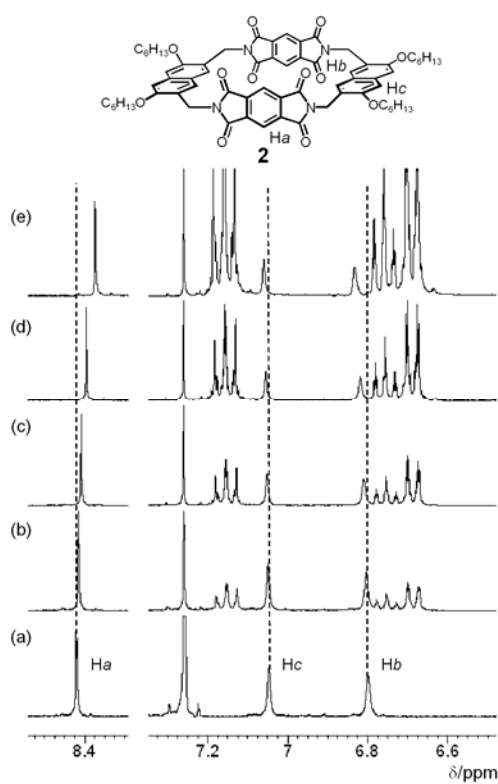


Figure S10. ^1H NMR observation of **2** recorded in CDCl_3 at 5×10^{-3} M (300 MHz, 25 °C) in the presence of (a) 0, (b) 2, (c) 5, (d) 10, or (e) 20 equiv of aniline.

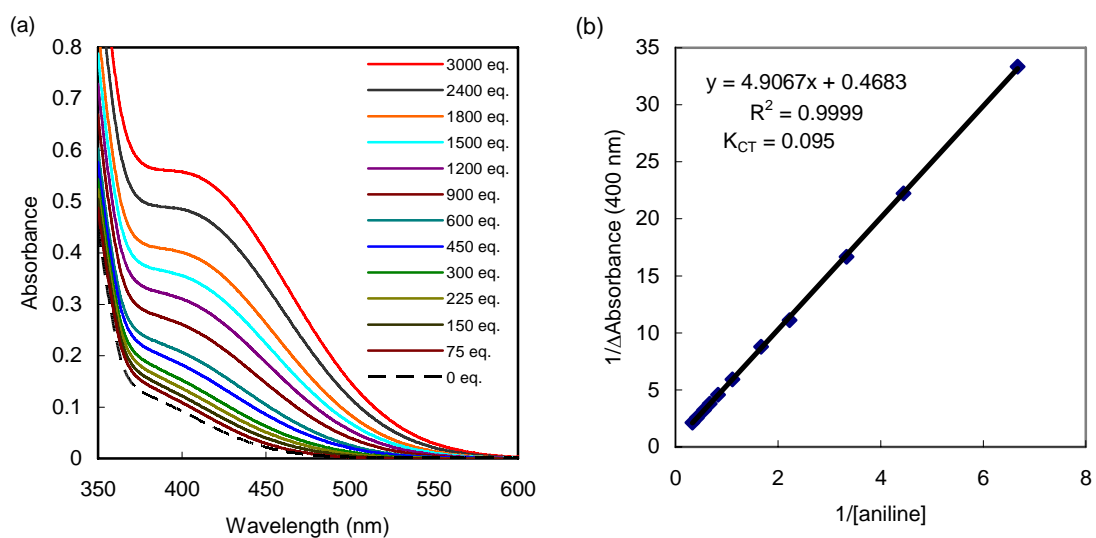


Figure S11. (a) Absorption spectra of **1** in CHCl₃ at 1 × 10⁻³ M in the presence of 0–3000 equiv of aniline. (b) Benesi-Hildebrand plot

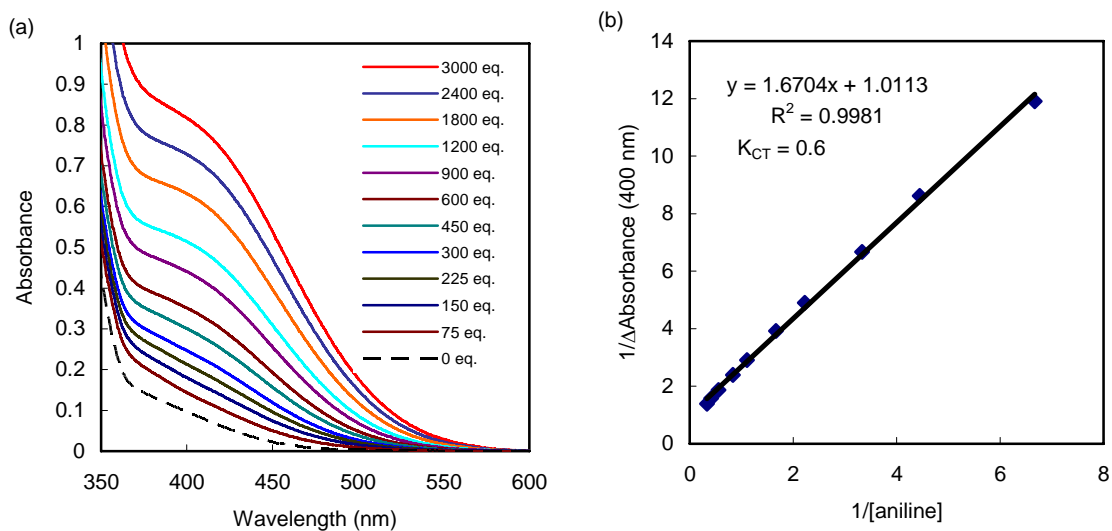


Figure S12. (a) Absorption spectra of **2** in CHCl₃ at 1 × 10⁻³ M in the presence of 0–3000 equiv of aniline. (b) Benesi-Hildebrand plot

6. Theoretical calculations^{S2}

Table S1. MP2/6-311++G**//B3LYP/6-311G** energetic data for the monomer, dimer, and trimer of aniline.

	number of monomers	total energy (a.u.)	relative energy per mol of aniline (kcal/mol)	number of hydrogen bonding
monomer	1	-285.803871314	0	0
dimer	2	-571.611539598	-1.191	2
N-H... π type cyclic trimer	3	-857.419855437	-1.723	3
N-H...N type cyclic trimer	3	-857.424391438	-2.672	3

Table S2. Coordinates of aniline.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.220261	1.205782	-0.004317
2	6	0	-1.170100	1.200202	0.003256
3	6	0	-1.878969	0.000001	0.007332
4	6	0	-1.170101	-1.200201	0.003256
5	6	0	0.220260	-1.205782	-0.004319
6	6	0	0.938343	0.000000	-0.007209
7	7	0	2.333300	-0.000002	-0.076328
8	1	0	0.759681	2.147956	-0.012704
9	1	0	-1.703237	2.144819	0.007014
10	1	0	-2.962283	0.000001	0.013865
11	1	0	-1.703238	-2.144819	0.007014
12	1	0	0.759679	-2.147957	-0.012710
13	1	0	2.779068	-0.836027	0.271931
14	1	0	2.779067	0.836039	0.271893

Table S3. Coordinates of aniline dimer.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.876071	1.137830	0.465880
2	6	0	2.970721	1.326589	-0.371901
3	6	0	3.820980	0.267049	-0.687021
4	6	0	3.558830	-0.988901	-0.141391
5	6	0	2.465880	-1.189990	0.694730
6	6	0	1.601190	-0.128840	1.011210
7	7	0	0.531270	-0.308960	1.882470
8	1	0	1.232541	1.974200	0.718260

9	1	0	3.162741	2.314439	-0.777181
10	1	0	4.673640	0.418699	-1.337701
11	1	0	4.211450	-1.825011	-0.369081
12	1	0	2.276739	-2.173520	1.113740
13	1	0	0.218650	-1.263509	1.983810
14	1	0	-0.248610	0.318211	1.739960
15	6	0	-2.466750	-1.198778	-0.679431
16	6	0	-3.559380	-0.986218	0.154290
17	6	0	-3.820530	0.276772	0.683860
18	6	0	-2.969529	1.331592	0.355160
19	6	0	-1.875249	1.131361	-0.480411
20	6	0	-1.601430	-0.142369	-1.009631
21	7	0	-0.531900	-0.334259	-1.878891
22	1	0	-2.278401	-2.187719	-1.085861
23	1	0	-4.212570	-1.818858	0.392810
24	1	0	-4.672940	0.437342	1.332720
25	1	0	-3.160739	2.324672	0.747850
26	1	0	-1.231119	1.963921	-0.743611
27	1	0	0.248870	0.293481	-1.743921
28	1	0	-0.220660	-1.290399	-1.968911

Table S4. Coordinates of N–H··· π type cyclic aniline trimer.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	0.973367	-2.557285	-0.754803
2	6	0	2.037982	-1.785877	-0.322613
3	6	0	3.087562	-1.445207	-1.195529
4	6	0	4.185807	-0.724173	-0.739770
5	6	0	4.273186	-0.317633	0.591899
6	6	0	3.235041	-0.651331	1.463385
7	6	0	2.130579	-1.370447	1.018730
8	1	0	0.123695	-2.522022	-0.209288
9	1	0	0.800240	-2.567479	-1.747768
10	1	0	3.040001	-1.763567	-2.232445
11	1	0	4.983145	-0.479460	-1.433510
12	1	0	5.131253	0.241953	0.943575
13	1	0	3.285445	-0.350328	2.504582
14	1	0	1.331454	-1.625788	1.706027
15	7	0	-2.782342	0.470079	-0.676133
16	6	0	-2.609052	-0.843532	-0.276045
17	6	0	-2.275146	-1.155166	1.054993
18	6	0	-2.167375	-2.479148	1.467738
19	6	0	-2.379808	-3.529750	0.573734
20	6	0	-2.708587	-3.227490	-0.748020
21	6	0	-2.821253	-1.907774	-1.171891

22	1	0	-2.704156	0.651833	-1.664572
23	1	0	-2.343694	1.185512	-0.113076
24	1	0	-2.108476	-0.348395	1.760647
25	1	0	-1.916135	-2.691295	2.501674
26	1	0	-2.294579	-4.558924	0.900251
27	1	0	-2.880793	-4.028339	-1.459290
28	1	0	-3.088242	-1.689596	-2.201395
29	7	0	1.813678	2.134506	-0.568486
30	6	0	0.574656	2.648778	-0.232113
31	6	0	0.072431	2.525368	1.076797
32	6	0	-1.144253	3.101497	1.426730
33	6	0	-1.900294	3.808483	0.490137
34	6	0	-1.409055	3.932039	-0.810027
35	6	0	-0.193377	3.362089	-1.171080
36	1	0	1.986831	1.978535	-1.548999
37	1	0	2.184077	1.397404	0.014899
38	1	0	0.650939	1.981751	1.815999
39	1	0	-1.504126	2.998450	2.445126
40	1	0	-2.846495	4.256117	0.768406
41	1	0	-1.977441	4.481366	-1.553095
42	1	0	0.179872	3.476823	-2.184117

Table S5. Coordinates of N–H···N type cyclic aniline trimer.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.925501	-3.216070	-1.327494
2	6	0	3.016998	-3.947659	-0.872540
3	6	0	3.434804	-3.853045	0.453926
4	6	0	2.738260	-3.014949	1.322407
5	6	0	1.643515	-2.280477	0.877345
6	6	0	1.221453	-2.371212	-0.457565
7	7	0	0.158682	-1.582023	-0.924443
8	1	0	1.613552	-3.293447	-2.364528
9	1	0	3.544818	-4.597218	-1.562388
10	1	0	4.285608	-4.424647	0.804833
11	1	0	3.044952	-2.932958	2.359573
12	1	0	1.102688	-1.637072	1.563419
13	1	0	-0.503176	-1.285011	-0.208120
14	1	0	-0.324958	-1.978856	-1.719274
15	6	0	-3.544681	0.481656	-0.755467
16	6	0	-4.879546	0.333321	-1.116852
17	6	0	-5.808859	-0.181851	-0.215013
18	6	0	-5.380580	-0.546005	1.060433
19	6	0	-4.047630	-0.403060	1.430341
20	6	0	-3.108607	0.114044	0.526357

21	7	0	-1.750338	0.201207	0.868912
22	1	0	-2.830393	0.891397	-1.461823
23	1	0	-5.195518	0.628045	-2.111829
24	1	0	-6.848215	-0.294024	-0.499436
25	1	0	-6.089842	-0.945519	1.777211
26	1	0	-3.725440	-0.695953	2.424864
27	1	0	-1.216104	0.891913	0.341486
28	1	0	-1.583445	0.291084	1.862253
29	6	0	1.372073	2.343802	-0.523877
30	6	0	2.396008	1.715927	0.199499
31	6	0	3.401482	2.472336	0.793191
32	6	0	1.385160	3.741015	-0.636195
33	6	0	2.396941	4.487528	-0.041827
34	6	0	3.411839	3.861381	0.679602
35	7	0	0.315680	1.592897	-1.071903
36	1	0	2.407126	0.634299	0.284161
37	1	0	4.187494	1.966919	1.343824
38	1	0	0.594499	4.240012	-1.188311
39	1	0	2.390087	5.567345	-0.143994
40	1	0	4.198980	4.445480	1.141365
41	1	0	0.527206	0.608722	-1.233185
42	1	0	-0.092873	2.014846	-1.895683

7. References

- S1 G. M. Sheldrick, SHELX-97, A Program for the Solution of Crystal Structures, University of Göttingen, Germany, 1997.
- S2 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian 03 revision C.02; Gaussian Inc.: Wallingford CT 2004.