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Electronic Supplementary Information

Selective Naked-eye Detection of Dopamine Using an Imino-Boron Molecular Capsule

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Experimental Section

General Experimental Conditions. All reactions were carried out in anhydrous organic solvents under an atmosphere of nitrogen. ^{1}H, ^{11}B and ^{19}F NMR spectra were recorded on a Bruker Avance II 500 MHz NMR spectrometer at 25 °C. NMR spectra were internally referenced to residual solvent signals: $CDCl_3$ was referenced at δ 7.26 ppm and DMSO-d_6 at δ 2.5 ppm. ^{11}B and ^{19}F NMR spectra in $CDCl_3$ were referenced using a sealed capillary containing 1% $BF_3.OEt_2$ as an internal standard where the reference peak positions for ^{11}B and ^{19}F were taken as δ −0.61 and −152.8 ppm, respectively.[1] ESI-MS spectra were measured on a Waters Q-Toff Micromass. Absorption spectra were recorded on a Shimadzu UV-2600 UV-visible spectrophotometer in 3 mL quartz cuvettes with a path length of 1 cm. Emission spectra were recorded on an Edinburg FS5 spectrofluorometer. Fluorescence quantum yield was calculated using fluorescein in 0.1 M NaOH as the reference standard.[2] Fluorescence lifetimes were measured by the time-correlated single-photon counting (TCSPC) technique on a Deltaflex modular fluorescence lifetime system from HORIBA Scientific using a nano-LED pulse diode light source. The instrument response function (IRF) of the setup was 200 ps and measured using 1% ludox (colloidal silica) solution. Absorption and emission spectra in the solid state were recorded by drop-casting a solution of the sample in chloroform on a glass slide and dried under vacuum. Electrochemical analysis was carried out at 25 °C in chloroform in a Metrohm Autolab electrochemical analyzer. Tetrabutylammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte. A standard three-electrode cell with a glassy carbon working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode was used for measurements. Samples were referenced with ferrocene as an internal standard.

Materials. Tris(2-amino)ethylamine, 4,4'-dihydroxybiphenyl, hexamethylenetetraamine, salicylaldehyde, trifluoroacetic acid, $BF_3.OEt_2$, diisopropylethylamine, dopamine hydrochloride, tropamine hydrochloride, adrenaline hydrochloride, noradrenaline hydrochloride and polymethylmethacylate (PMMA) were purchased from Sigma-Aldrich. Triethylamine and 1,4-dioxane were purchased from Qualigens. Fetal bovin serum (FBS) was purchased from HiMedia. Analytical thin layer chromatography (TLC) from Merck was used for monitoring the reactions. Silica gel 100-200 mesh and solvents for purification were

purchased locally and distilled prior to use. Spectroscopic grade solvents were purchased from Merck and dried with appropriate drying agent prior to use. For molecular recognition experiments, stock solutions of the hydrochloride salt of the neurotransmitter molecules were prepared in 50% chloroform-methanol and aliquots were added to a solution of 4 or 7 in 50% chloroform-methanol.

Syntheses.

Synthesis of 2.[3] 4,4'-Dihydroxybiphenol **1** (3 g, 16 mmol) and hexamethylenetetraamine were dissolved in trifluoroacetic acid (35 mL) and stirred for 3 hours at 110 ^{o}C. After cooling the reaction mixture it was poured in to 4N HCl (350 mL) and stirred overnight. The yellow solid was collected by filtration, washed with water (3 × 100 mL), dried overnight under vacuum, and purified by column chromatography using a mixture of 15% ethyl acetate in hexane as eluting agents to afford 1.0 g of **2** as pale yellow solid (28%). ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm) 10.82 (s, 2H), 10.32 (s, 2H), 7.89 (d, *J* = 5 Hz, 2H), 7.83 (dd, *J* = 5 Hz, *J* = 5 Hz, 2H), 7.09 (d, *J* = 10 Hz, 2H); IR (cm^{-1}): 1650 (s), 1467 (s), 1374 (w), 1348 (w), 1275 (s), 1230 (m), 1179 (m), 1132 (m), 1046 (m), 884 (m), 834 (w), 765 (w), 684 (w); GC-MS m/z calculated for $C_{14}H_{10}O_4$ $(M)^+$: 242.06, found: 242.10.

Synthesis of 3. To a stirred solution of **2** (100 mg, 0.41 mmol) in dry 1,4-dioxane (100 mL), 2-amino)ethylamine (41.5 mL, 0.27 mmol) was added under an atmosphere of nitrogen and refluxed at 60 ^{o}C for 3 days. After cooling to room temperature, dioxane was evaporated and the reaction mixture was dissolved in dichloromethane (100 mL), washed with water (3 × 25 mL) and brine (20 mL). The organic layers were collected, dried over anhydrous sodium sulfate, filtered and evaporated to get a yellow residue. The crude product was purified by column chromatography over silica gel using a mixture of 1% methanol in chloroform to afford compound **3** in 80% yield. M.p. 218-220 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 14.26 (br s, 6H), 7.89 (s, 6H), 7.06 (d, *J* = 2.0 Hz, 12H), 5.91 (d, *J* = 2 Hz, 6H), 3.83-3.80 (d, *J* = 15 Hz, 6H), 3.36-3.30 (t, *J* = 15 Hz, 6H), 3.04-2.98 (t, *J* = 15 Hz, 6H), 2.83-2.79 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 166.5, 160.5, 131.6, 129.9, 127.6, 118.6, 116.7, 58.1, 55.6; IR (cm^{-1}): 1628 (s), 1586 (m), 1472 (s), 1277 (s), 1230 (m), 1180 (m), 1119 (m), 809 (w), 520 (w); HRMS (ESI-MS): m/z calculated for $C_{54}H_{55}N_8O_6$ [M+H$^+$], 911.4245, found 911.4243.

Synthesis of 4. To a stirred solution of **3** (60 mg, 0.065 mmol) in dry toluene (60 mL) at 40 ^{o}C under an atmosphere of nitrogen, diisopropylethylamine (1.56 mL, 9 mmol) was added. After stirring for 30 minutes, $BF_3.OEt_2$ (2.21 mL, 18 mmol) was added drop wise and the reaction mixture was stirred for another 4 hours under nitrogen. *n*-Pentane was added to the cooled reaction mixture and the precipitate formed was collected, washed with water (2 × 25 mL) and dried under vacuum. The crude product was purified by column chromatography over silica gel using a mixture of 5% methanol in chloroform to afford compound **4** in 75% yield. M.p. 256-258 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.89 (br s, 6 H), 7.05 (dd, *J* = 4 Hz, *J* = 2 Hz, 12 H), 5.92-5.91 (m, 6H), 3.81 (d, *J* = 15 Hz, 6H), 3.36-3.30 (t, *J* = 15 Hz, 6H), 3.03-2.97 (t, *J* = 15 Hz, 6H), 2.83-2.79 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 167, 161, 132, 130, 128, 119, 117, 58, 56; ^{19}F NMR (472 MHz, $CDCl_3$) δ (ppm) –132.18, –145.96; ^{11}B NMR (160 MHz, $CDCl_3$) δ (ppm) –0.14 (t, *J* = 16 Hz); IR (cm^{-1}): 1618 (s), 1504 (s), 1471 (s), 1284 (m), 1183 (m), 814 (w), 511 (w); HR-MS: m/z calculated for $C_{54}H_{49}B_6F_{12}N_8O_6$ [M+H^{+}], 1199.4142, found 1199.4140.

Synthesis of 6.[4] To a stirred solution of tris(2-amino)ethylamine (0.25 mL, 1.71 mmol) in dry ethanol (60 mL), salicylaldehyde **5** (0.62 mL, 5.64 mmol) was added and the reaction mixture was refluxed at 60 ^{o}C for 3 hours in the presence of catalytic amounts of acetic acid. The reaction mixture was cooled to room temperature, the precipitate formed was collected and purified by column chromatography over silica gel using a mixture of 40% chloroform in hexane to afford compound **6** in 80% yield. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 13.60 (br s, 3H), 8.25 (br s, 3H), 7.32-7.28 (m, 3H), 6.90 (dd, *J* = 10 Hz, *J* = 5 Hz, 3H), 6.85 (br s, 3H), 6.77-6.74 (m, 3H), 3.6 (t, *J* = 5 Hz, 6H), 2.84 (t, *J* = 5 Hz, 6H); IR (cm^{-1}): 1623 (s), 1508 (s), 1480 (s), 1276 (m), 1179 (m), 807 (w), 519 (w).

Synthesis of 7.[4] To an ice-cold stirred solution of **6** (100 mg, 0.21 mmol) in dry dichloromethane (100 mL) under an atmosphere of nitrogen, triethylamine (0.13 mL, 0.94 mmol) was added and stirred for 30 minutes. To this $BF_3.OEt_2$ (0.23 mL, 1.89 mmol) was added and reaction was stirred for another 6 hours. The precipitated white residue was collected, washed with dichloromethane (2 × 50 mL), water (2 × 30 mL) and dried under vacuum to yield 88% of **7**. ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm) 8.77 (br s, 3H), 7.66-7.63 (m, 3H), 7.45 (dd, *J*

= 10 Hz, *J* = 5 Hz, 3H), 7.00 (m, 6.85, 3H), 3.78 (t, *J* = 5 Hz, 6H), 3.00 (t, *J* = 5Hz, 6H); IR (cm^{-1}): 1618 (s), 1572 (s), 1474 (s), 1276 (m), 1145 (m), 812 (w), 544 (w).

Calculation of change in free energy (ΔG_{ET}) for photoinduced electron transfer. The change in free energy (ΔG_{ET}) for the photoinduced electron transfer reaction was evaluated according to Rehm-Weller equation[5,6]:

$$\Delta G_{ET} = E_{ox} - E_{red} - w_p - E_{(0,0)}$$

where, $E_{(0,0)}$ is the singlet excitation energy in eV, w_p is the work term, E_{ox} is the oxidation potential of the donor and E_{red} is the reduction potential of the acceptor. The oxidation potential and the singlet state energy of the capsule were measured as 1.06 V and 2.84 eV, respectively by cyclic voltammetry (Fig. S25) and UV-Vis absorption spectroscopy. The reduction potential of the neurotransmitters was taken as –0.1, –0.24 and –0.17 V for dopamine, adrenaline and noradrenaline, respectively from the literature.[7–9] The work term w_p was taken as 0 for calculations as the molecules under study were neutral. The change in free energy (ΔG_{ET}) for electron transfer from the neurotransmitters to the molecular capsule was found to be –1.68, –1.54 and –1.61 eV for dopamine, adrenaline and noradrenaline, respectively.

Chemosensing through UV-Visible spectroscopy

Solutions of compounds **4** (10 μM) and **7** (15 μM) and biogenic amines (750 μM) were made in 1:1 chloroform-methanol mixture. The biogenic amines were titrated against compounds **4** and **7**. The absorption spectra were recorded using Shimadzu double beam spectrophotometer, UV-2600. The titration continued till a saturation point was observed.

Chemosensing through fluorescence spectroscopy

Solutions of compounds **4** (10 μM) and **7** (15 μM) and biogenic amines (750 μM) were prepared in 1:1 chloroform-methanol mixture. The biogenic amines were titrated against compounds **4** and **7** and the emission spectra were recorded on an Edinburg FS5 spectrofluorometer with a slit width of 5 nm. The titration was continued till a saturation point was observed.

Determination of stoichiometry of complex by Jobs method

A series of solutions containing compound **4** (10 μM) and dopamine (10 μM) were prepared in 1:1 chloroform-methanol mixture. The mole fraction of **4** was varied from 0.1 to 1, and the changes in absorbance were plotted against the mole fraction.

Determination of binding constant using Benesi-Hildebrand method

The association constant of **4** with dopamine was determined by UV-Visible spectroscopy by employing the Benesi-Hildebrand method.[10,11]

$$1/ A_0\text{-}A = 1/(A0\text{-}A_\infty)K[G]+ 1/(A0\text{-}A_\infty)$$

where A and A_0 are the absorbance of **4** with and without dopamine, and A_∞ is the absorbance for infinite dilution of **4** with dopamine.

Determination of LOD

The LOD of **4** for dopamine was calculated as

$$LOD = K*S_b/k.$$

where K = 3, S_b and k represent the standard deviation of ligand solution and slope obtained from the calibration plot.

Preparation of thin films. A 2.6 wt% solution of polymethylmethacrylate (PMMA) was prepared in chloroform, and this solution was used to prepare a solution of the imino-boron capsule **4** (0.23 mM). 2 mL of this solution was drop-casted on a glass surface, and the solvent was allowed to evaporate under ambient conditions for 12 hours. The thin film thus formed was peeled off and used for chemosensing experiments.

Computational Methods. *Ab initio* molecular dynamics (AIMD) simulations were performed using SIESTA software package[12] with the GGA approximation in the form of PBE functional.[13] A production trajectory of 4 ps was generated with a 1 fs time step in the NVT ensemble employing Nose-Hover thermostat. The temperature was set to 300 K. The DZP basis set and norm-conserving pseudopotentials were used to treat the valence and core orbitals of all the molecular atoms.[14] A mesh cut-off of 200 Ry was used and the convergence tolerance for the SCF density matrix was set to 10^{-4} eV. The initial geometry of the capsule **4** used in AIMD simulations was obtained from BLYP/def2-SVP optimization using ORCA package.[15] All the

guest molecules were first optimized using B3LYP/def2-TZVP method[16], which were then encapsulated in the capsule structure for simulations.

Table S1. Comparison of various sensors developed for dopamine sensing.

Entry	Material used	Medium	Method of detection	LOD	Ref
1	Thiacalixarene	MeOH	Fluorescence	0.1 mM	New J. Chem., 2018, 42, 177-183
2	β-Cyclodextrin-capped ZnO-doped carbon dot	Water and phosphate buffer	Fluorescence	285 nM	New J. Chem., 2021,45, 21299-21307
3	Boron and sulfur co-doped graphene quantum dots	PBS buffer	Fluorescence	3.6 µM	Scientific Rep. 2022, 12, 9061
4	Chitosan/graphene quantum dots	Water	Surface plasmon resonance	1.0 fM	Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2021, 263, 120202
5	CD-f-PEDOT: PSS sensor	Phosphate buffer	Electrochemical	9.596 nM	Sensors and Actuators B: Chemical, 2018, 255, 1655-1662
6	Boronic acid polymer sensors	Ethanol	Fluorescence	4×10^{-5} M	Sensors and Actuators B: Chemical, 2017, 253, 987-998
7	Terbium(III) metal-organic framework	Tris-HCl	Fluorescence	0.41 µM	Talanta 2021, 221, 121399
8	Tyr@PANI/CNTs/CNC conductive film	In 5 mM $[K_3(FeCN_6)^{3-/4-}$	CV	1.57 nM	ChemistrySelect, 2020, 5, 12470-12476

9	[Eu(pzdc)(Hpzdc)(H_2O)]n MOF	Buffer	Fluorescence	21 nM	ACS Appl. Mater. Interfaces 2020, 12, 40, 44499-44507
10	Imino-boron molecular capsule **4**	$CHCl_3$/MeOH (1:1)	Fluorescence	1.2 µM	Present study

Table S2. Diffusion coefficients of dopamine, molecular capsule **4** and a mixture of dopamine and **4** in 1:1 $CDCl_3$-CD_3OD (400 MHz, 298 K).

Compound	D (10^{-10} m^2s^{-1})
4	6.22
Dopamine	5.87
Dopamine + **4**	1.19

References

1 E. L. Myers, C. P. Butts and V. K. Aggarwal, *Chem. Commun.*, 2006, 4434–4436.

2 A. M. Brouwer, *Pure Appl. Chem.*, 2011, **83**, 2213–2228.

3 M. W. Schneider, I. M. Oppel and M. Mastalerz, *Chem. Eur. J.*, 2012, **18**, 4156–4160.

4 X. Zhang, J. Shi, J. Song, M. Wang, X. Xu, L. Qu, X. Zhou and H. Xiang, *ACS Omega*, 2018, **3**, 8992–9002.

5 A. Weller, *Zeitsch. Physikal. Chem.*, 1982, **133**, 93–98.

6 D. Rehm and A. Weller, *Ber. Bunsenges Phys. Chem.*, 1969, **73**, 834–839.

7 D. F. de Queiroz, T. R. de L. Dadamos, S. A. S. Machado and M. A. U. Martines, *Sensors*, 2018, **18**, 1223.

8 D. H. Kim, Y. Oh, H. Shin, C. D. Blaha, K. E. Bennet, K. H. Lee, I. Y. Kim and D. P. Jang, *J. Electroanal. Chem.*, 2014, **717–718**, 157–164.

9 C. V. Krishnan and M. Garnett, *Int. J. Electrochem. Sci.*, 2006, **1**, 283–303.

10 I. D. Kuntz, F. P. Gasparro, M. D. Johnston and R. P. Taylor, *J. Am. Chem. Soc.*, 1968, **90**, 4778–4781.

11 H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, 1949, **71**, 2703–2707.

12 J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón and D. Sánchez-Portal, *J. Phys.: Condens. Matter*, 2002, **14**, 2745–2779.

13 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.

14 N. Troullier and J. L. Martins, *Phys. Rev. B*, 1991, **43**, 1993–2006.

15 F. Neese, *WIREs Comput. Mol. Sci.*, 2012, **2**, 73–78.

16 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.

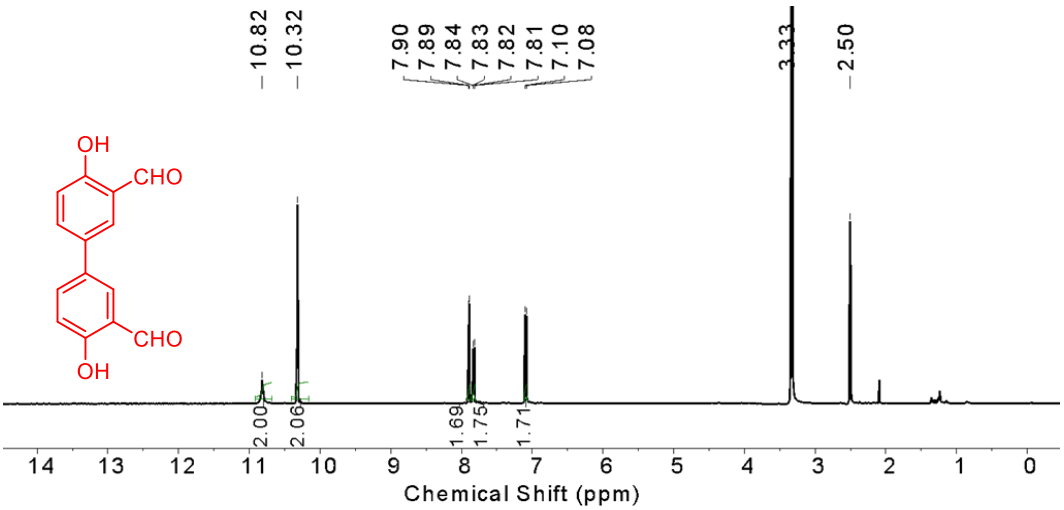


Fig. S1. ^{1}H NMR spectrum of **2** in DMSO-d_6 at 298 K.

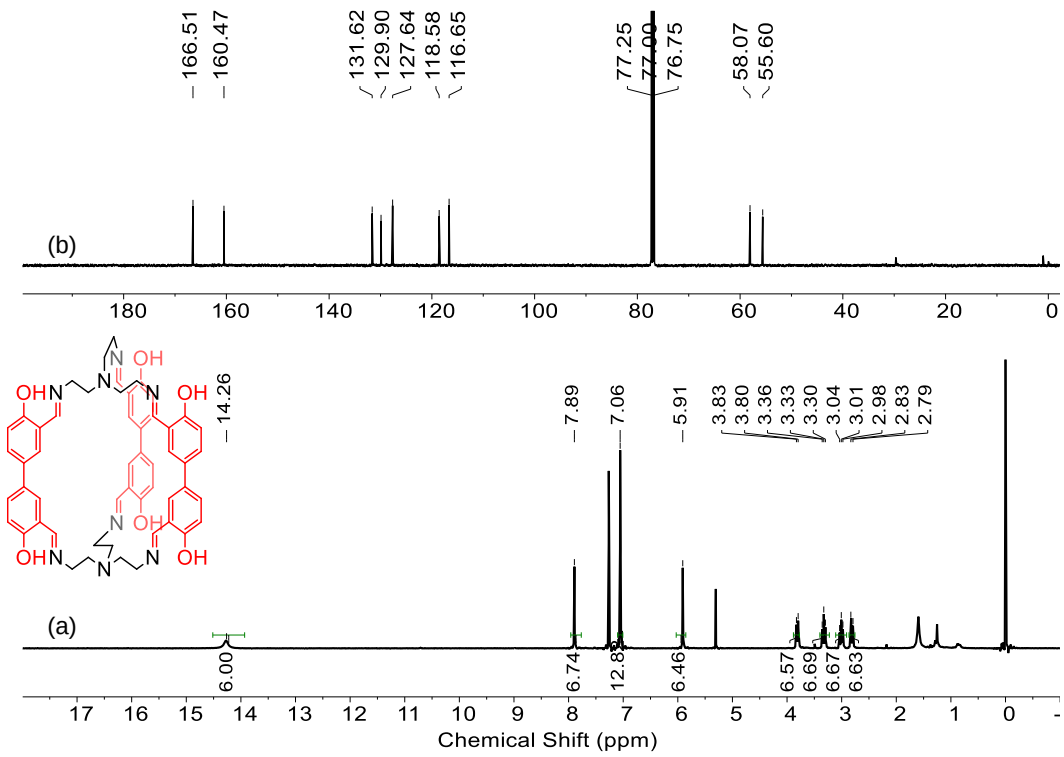
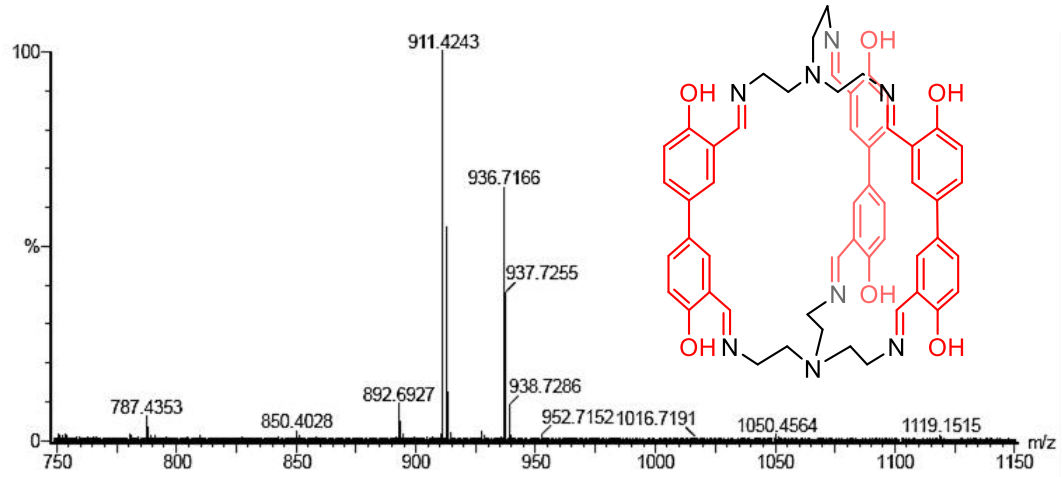


Fig. S2. (a) ^{1}H and (b) ^{13}C NMR spectra of **3** in $CDCl_3$ at 298 K.



Minimum:			-1.5				
Maximum:		5.0	50.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%) Formula
911.4243	911.4245	-0.2	-0.2	31.5	528.7	n/a	n/a C54 H55 N8 O6

Fig. S3. High-resolution mass spectrum (ESI-MS) of **3**.

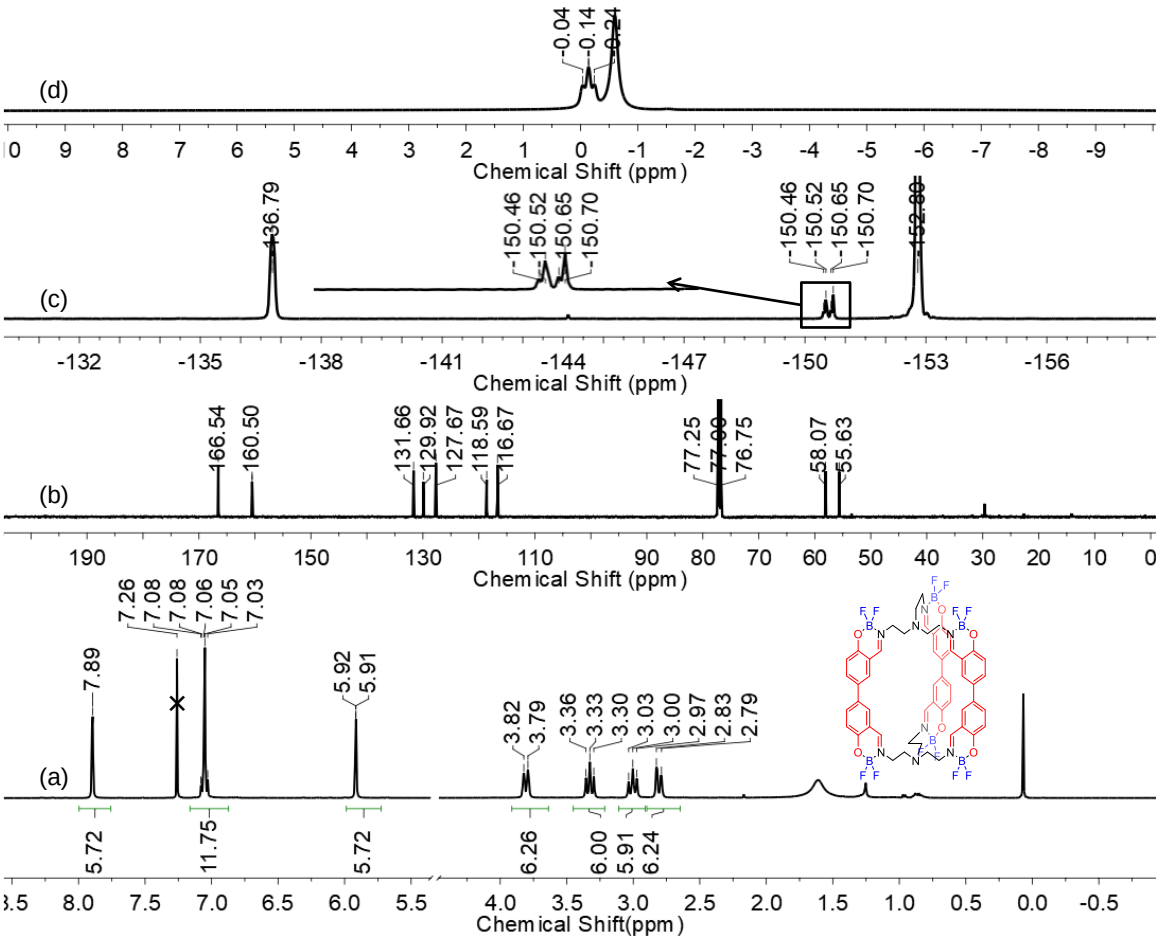


Fig. S4 (a) ^{1}H, (b) ^{13}C (c) ^{19}F and (d) ^{11}B NMR spectra of **4** in $CDCl_3$ at 298 K.

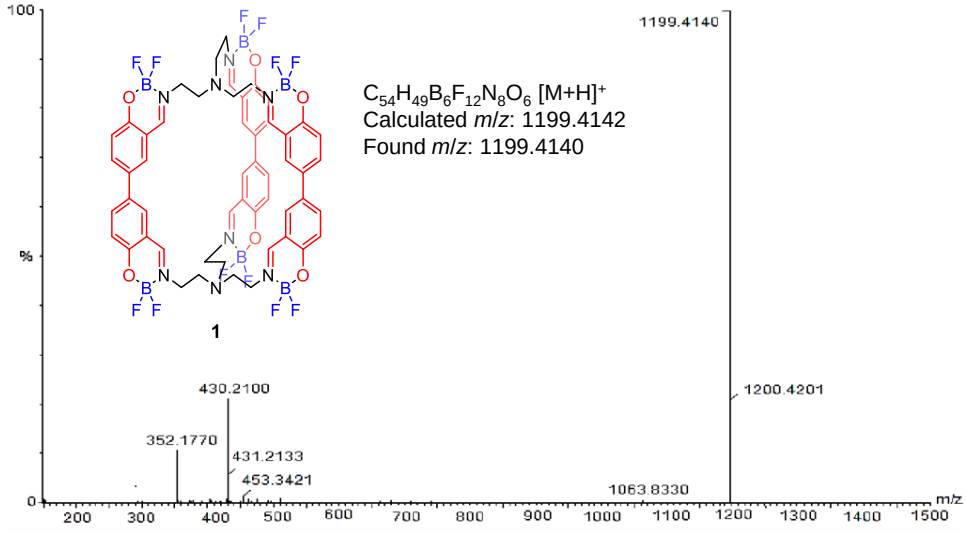


Fig. S5. High-resolution mass spectrum (ESI-MS) of **4**.

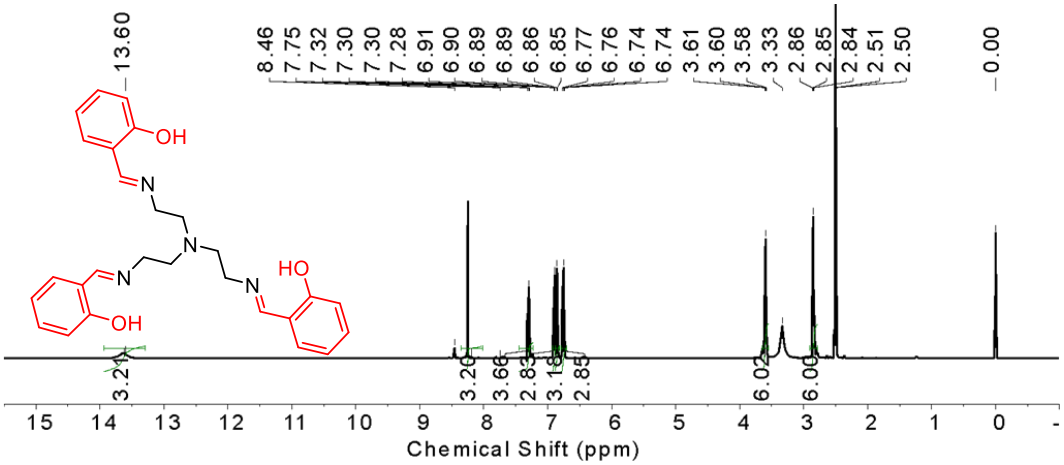


Fig. S6. ^{1}H NMR spectrum of **6** in DMSO-d_6 at 298 K.

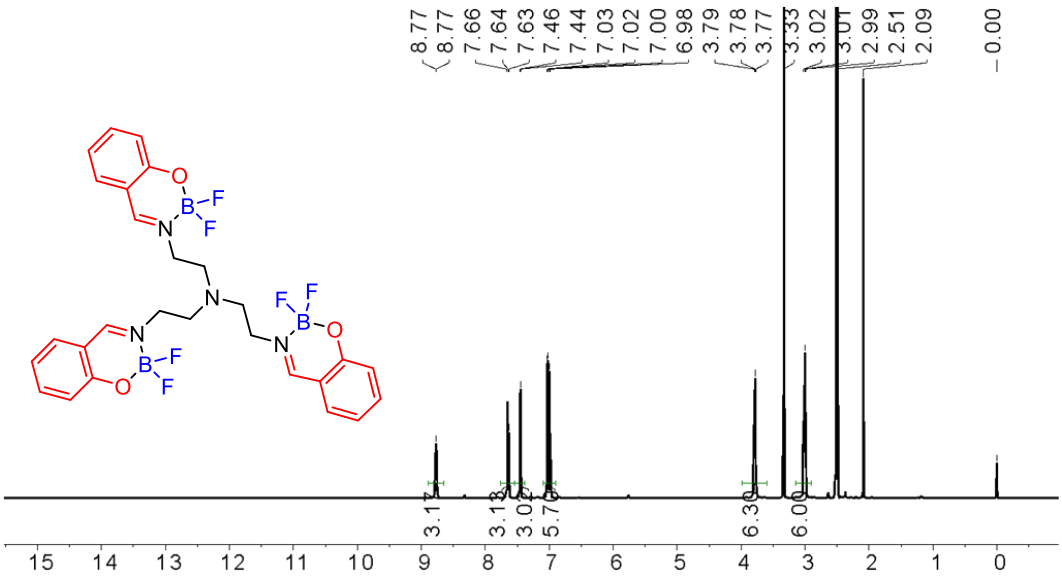


Fig. S7. ^{1}H NMR spectrum of **7** in DMSO-d_6 at 298 K.

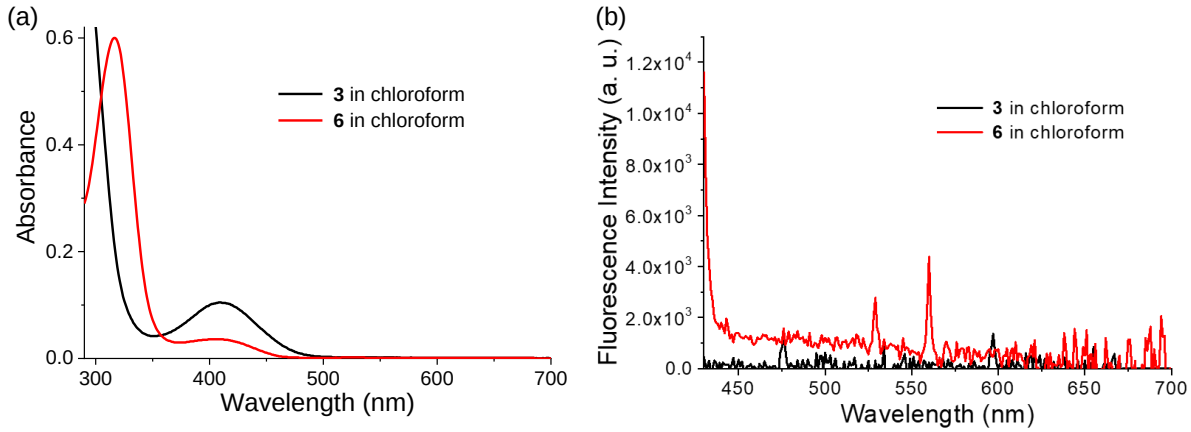


Fig. S8. (a) Absorption and (b) emission spectra of the precursor imine molecules **3** (10 µM) and **6** (15 µM) in chloroform. Excitation wavelength, 420 nm.

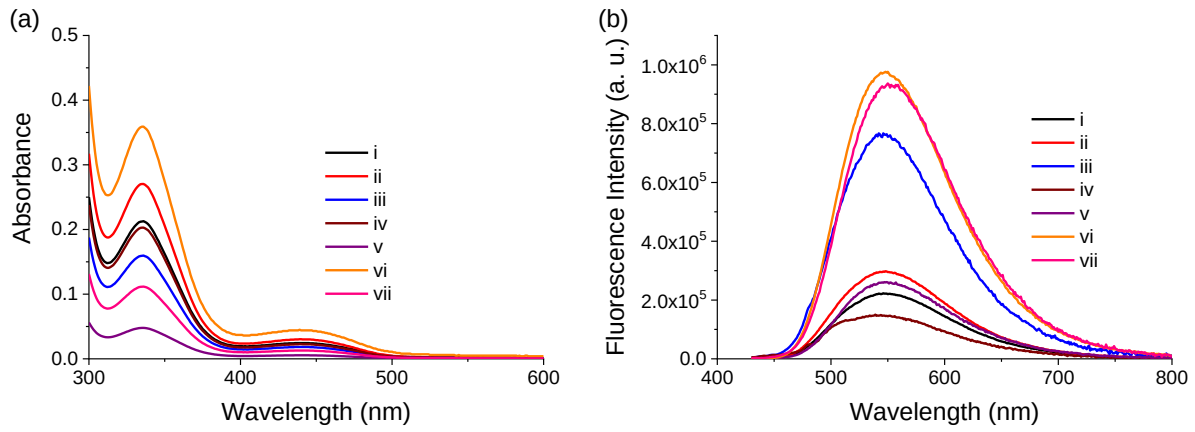


Fig. S9. (a) Absorption and (b) emission spectra of **4** (10 µM) in (i-vii) methanol, acetonitrile, dimethylsulfoxide, acetone, tetrahydrofuran, chloroform, and 50% chloroform-methanol. Excitation wavelength, 420 nm.

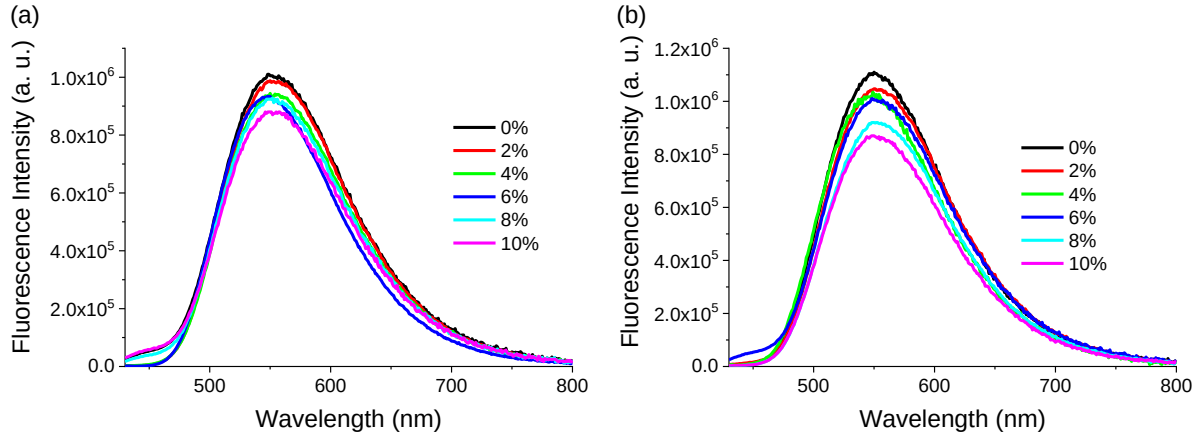


Fig. S10. Fluorescence spectra of **4** (10 µM) in the presence of varying amounts of (a) trifluoroacetic acid and (b) triethylamine in chloroform. Excitation wavelength, 420 nm.

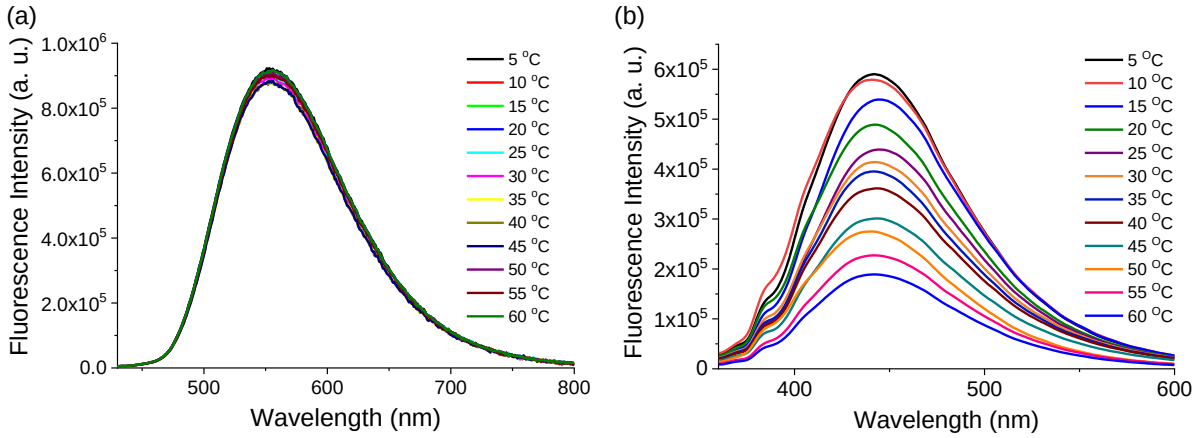


Fig. S11. Emission spectra of (a) **4** (10 µM) and (b) **7** (15 µM) in chloroform at various temperatures. Excitation wavelength, 420 and 350 nm for **4** and **7**, respectively.

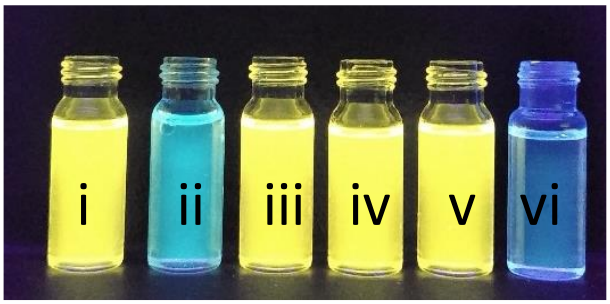


Fig. S12. Photograph showing the visual fluorescence of (i) **4** (10 µM) and (ii-vi) **4** (10 µM) in the presence of dopamine (28 µM), tropamine (75 µM), adrenaline (75 µM) and noradrenaline (75 µM), respectively in 50% chloroform-methanol. (vi) Visual fluorescence of **4** (10 µM) in the presence of dopamine (28 µM), tropamine (75 µM), adrenaline (75 µM) and noradrenaline (75 µM) in 50% chloroform-methanol.

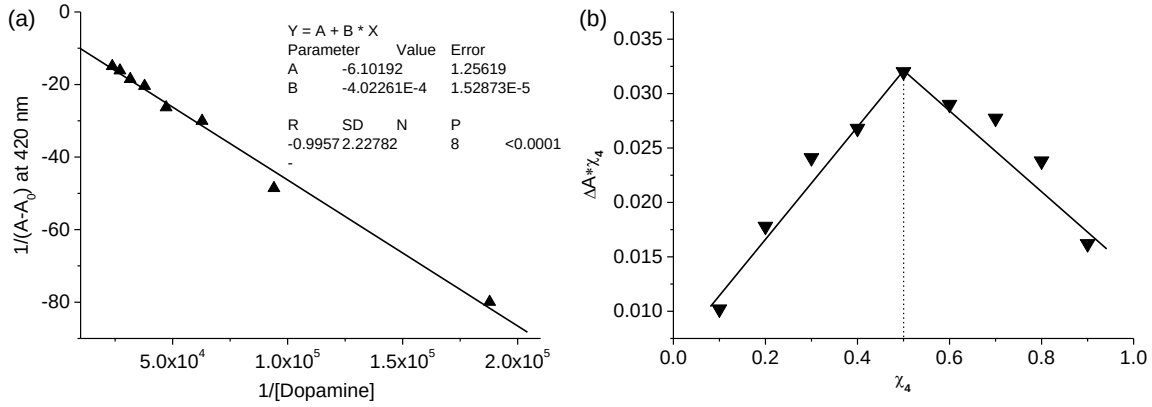


Fig. S13. (a) Benesi-Hildebrand analysis of the changes in the absorbance of **4** (10 µM) in the presence of dopamine (0-75 µM) at 420 nm in 50% chloroform-methanol. (b) Job's plot for the interaction between **4** and dopamine in 50% chloroform-methanol.

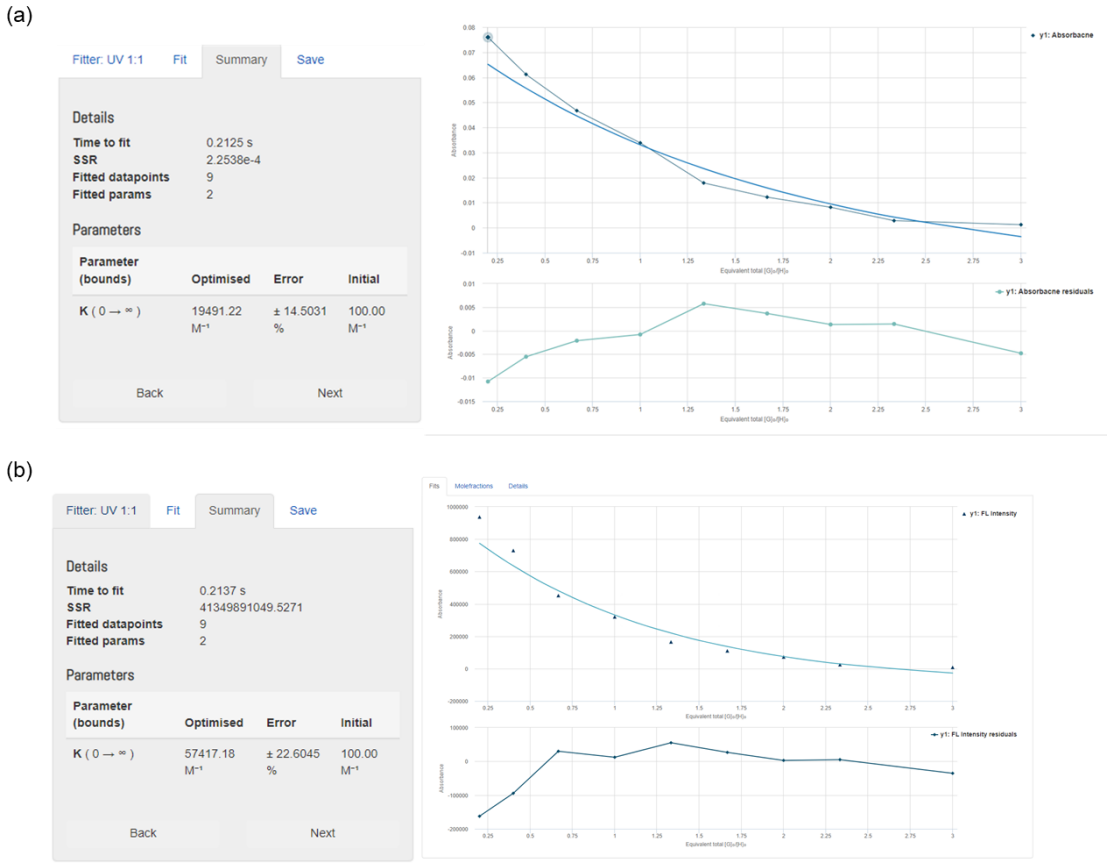


Fig. S14. Screenshots taken from the summary window of the website supramolecular.org. This screenshots shows the raw data for titration of **4** with dopamine and the data fitted to 1:1 binding model using (a) absorption and (b) emission titration data.

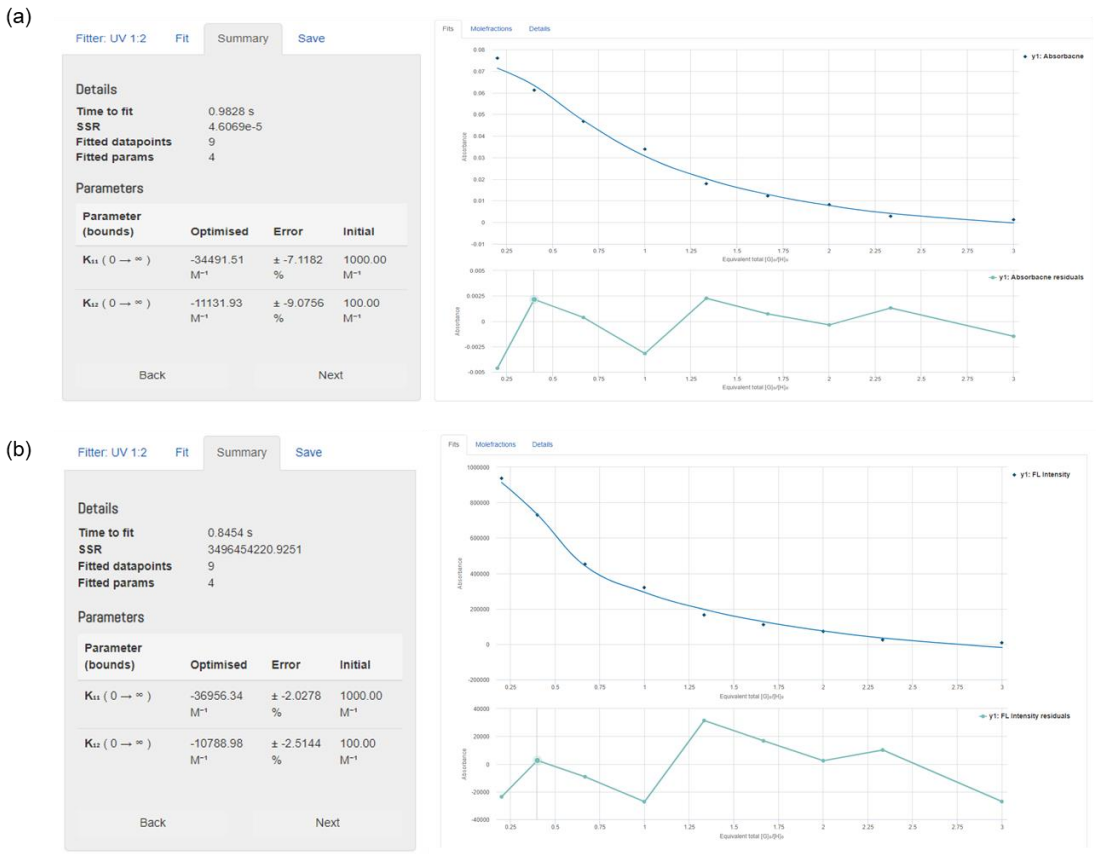


Fig. S15. Screenshots taken from the summary window of the website supramolecular.org. This screenshot shows the raw data for titration of **4** with dopamine and the data fitted to 1:2 binding model using (a) absorption and (b) emission titration data.

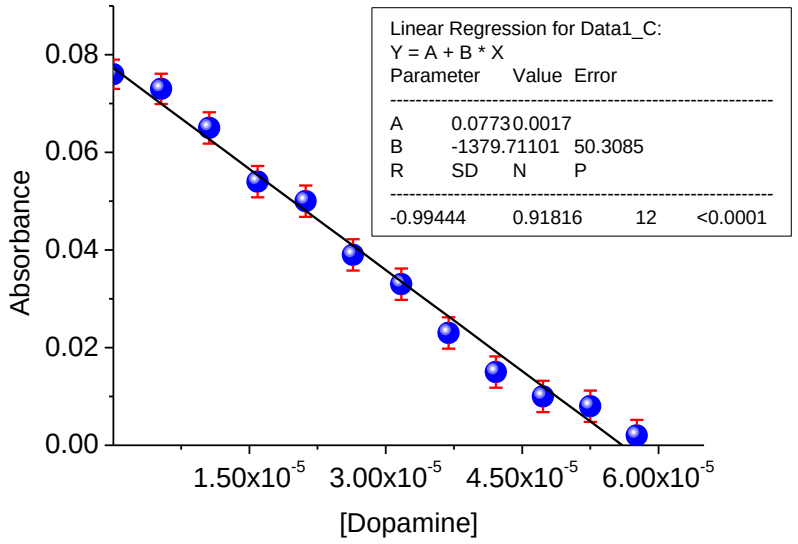


Fig. S16. Calibration plot for determining the limit of detection of dopamine by **4** for a concentration range from 0.05 to 60 µM.

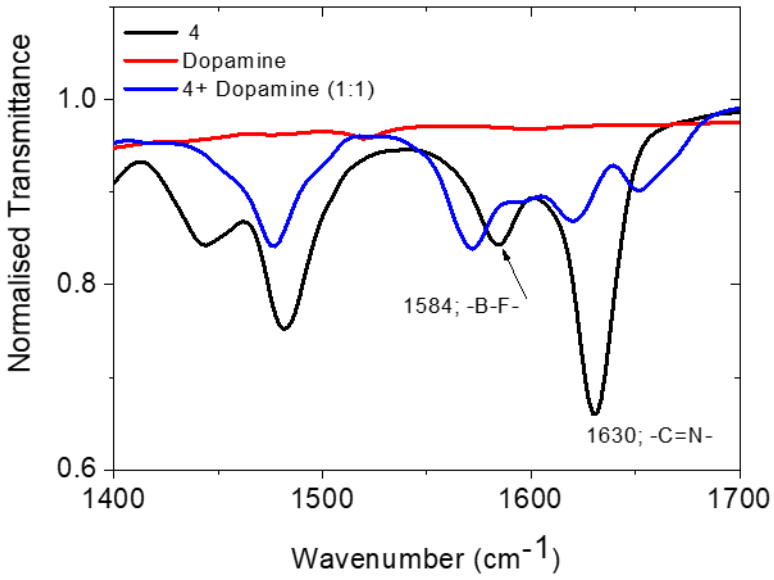


Fig. S17. FTIR spectra of **4**, dopamine and 1:1 complex of **4** and dopamine in 50% $CHCl_3$/MeOH.

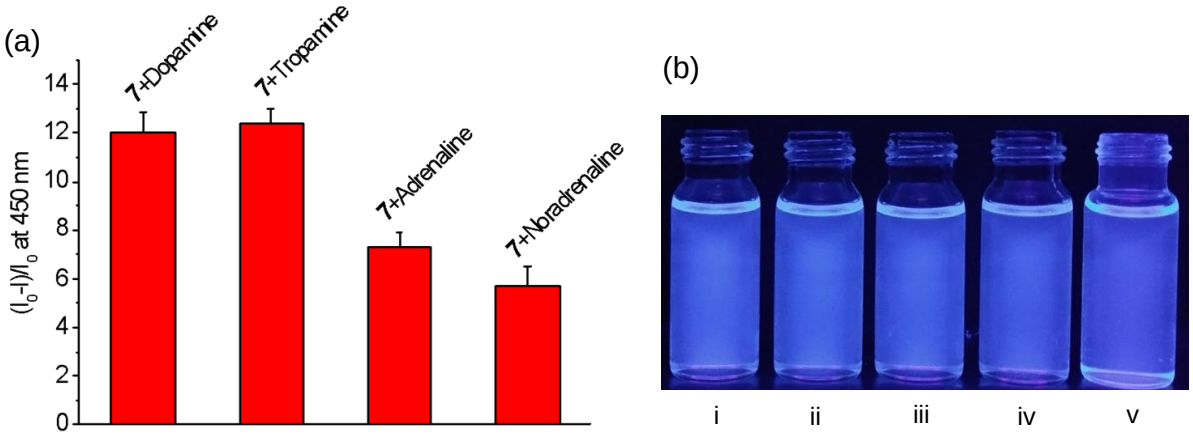


Fig. S18. (a) Relative changes in fluorescence of **7** (15 µM) at 450 nm in the presence of 850 µM of different neurotransmitters in 50% chloroform-methanol. (b) Photograph showing the fluorescence of (i) **7** (15 µM) and (ii-v) **7** in the presence of dopamine (850 µM), tropamine (850 µM), adrenaline (850 µM), and noradrenaline (850 µM), respectively, in 50% chloroform-methanol viewed under a UV lamp. Excitation wavelength, 350 nm.

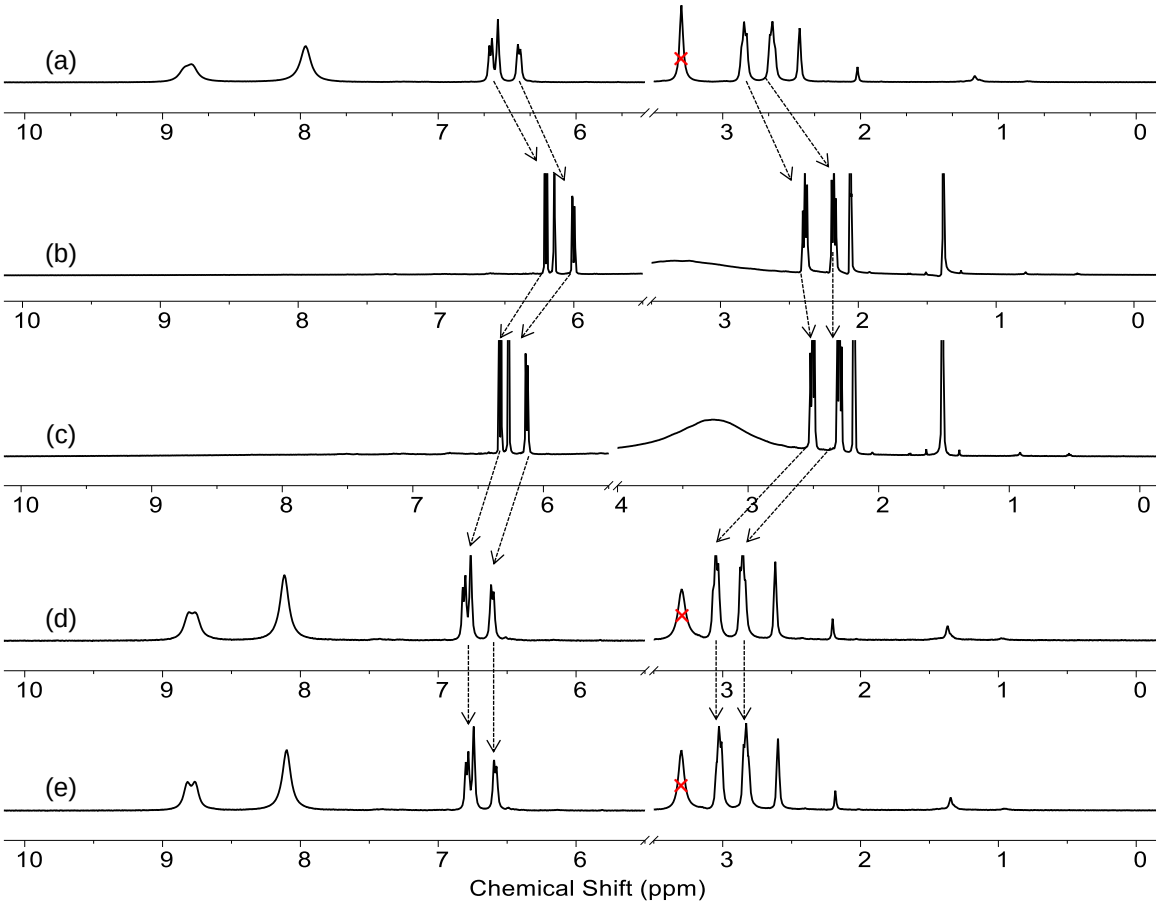


Fig. S19. ^{1}H NMR spectrum of (a) dopamine and dopamine in the presence of the capsule **4** at (b) 25, (c) 35, (d) 45 and (e) 55 °C in DMSO-d_6. [Dopamine] = 11.6 mM, [**4**] = 4 mM.

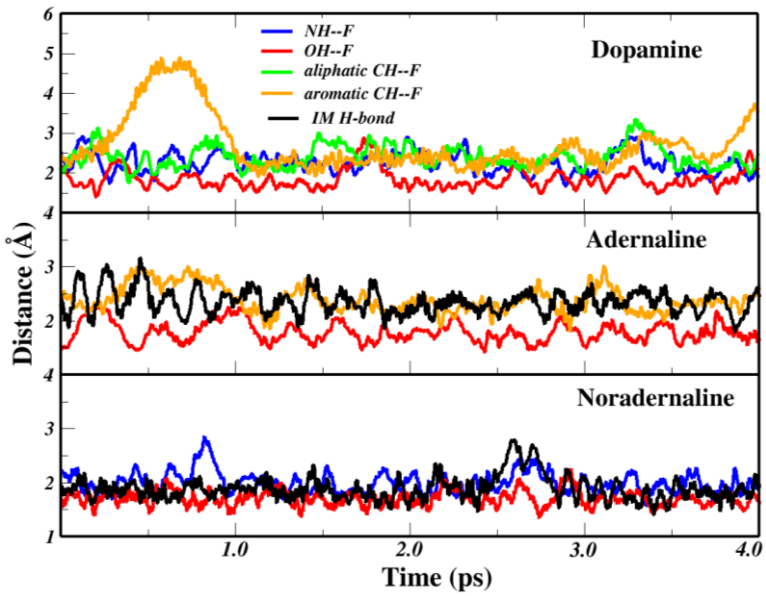


Fig. S20. Variation of the possible H-bonding distances along the MD-trajectory. For dopamine, maximum number of H-bonding interactions with the capsule was observed as compared to adrenaline and noradrenaline. For adrenaline and noradrenaline, lesser number of H-bonding interactions of comparable strength was observed with the capsule accompanied by competitive intramolecular hydrogen bonds (shown by black curve).

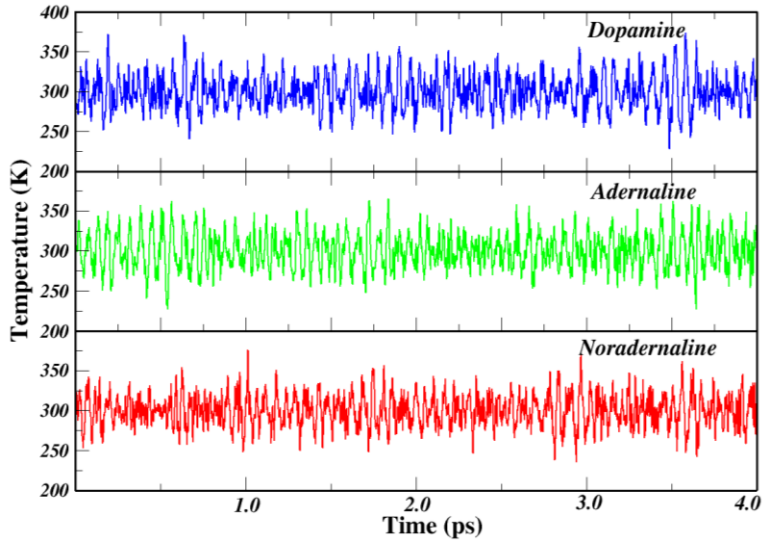


Fig. S21. Temperature fluctuations for dopamine, adrenaline and noradrenaline in the capsule structure from the simulation of 4 ps trajectory obtained after equilibration run indicating the thermal equilibration of the systems. The average temperature is 300 K.

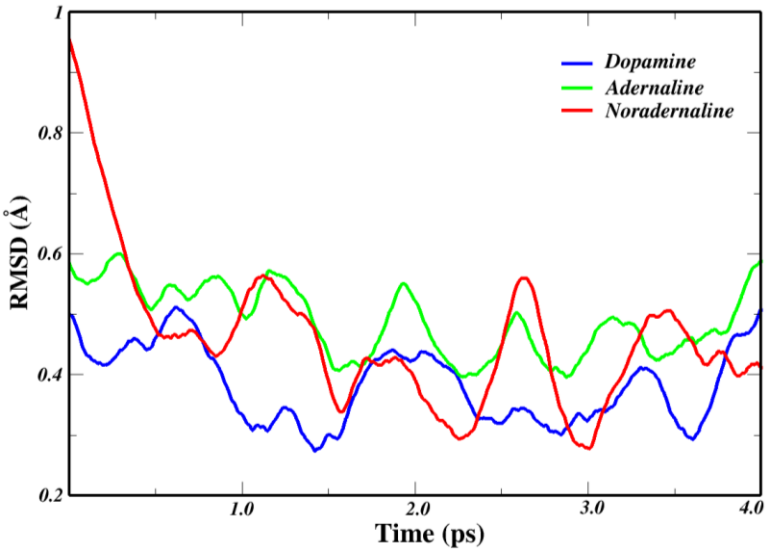


Fig. S22. Structural fluctuations in MD simulations as captured by RMSD during 4 ps production dynamics for dopamine (blue), adrenaline (green) and noradrenaline (red) in the cavity of the capsule **4**.

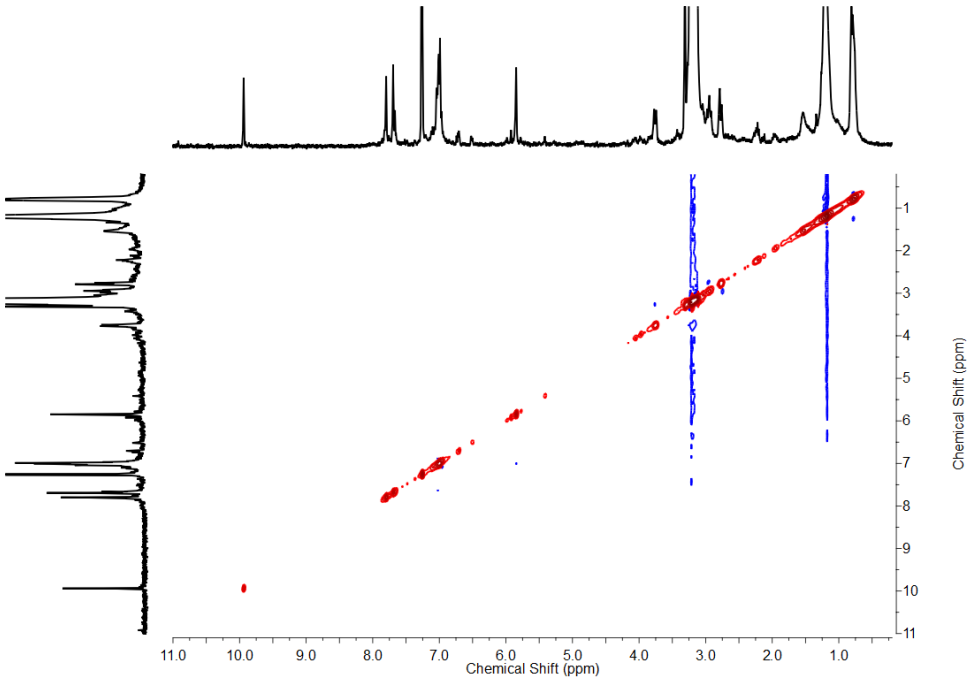


Fig. S23. ^{1}H-^{1}H NOESY spectrum of a mixture of **4** (5 mM) and dopamine (33 mM) in 50% $CDCl_3$-CH_3OD.

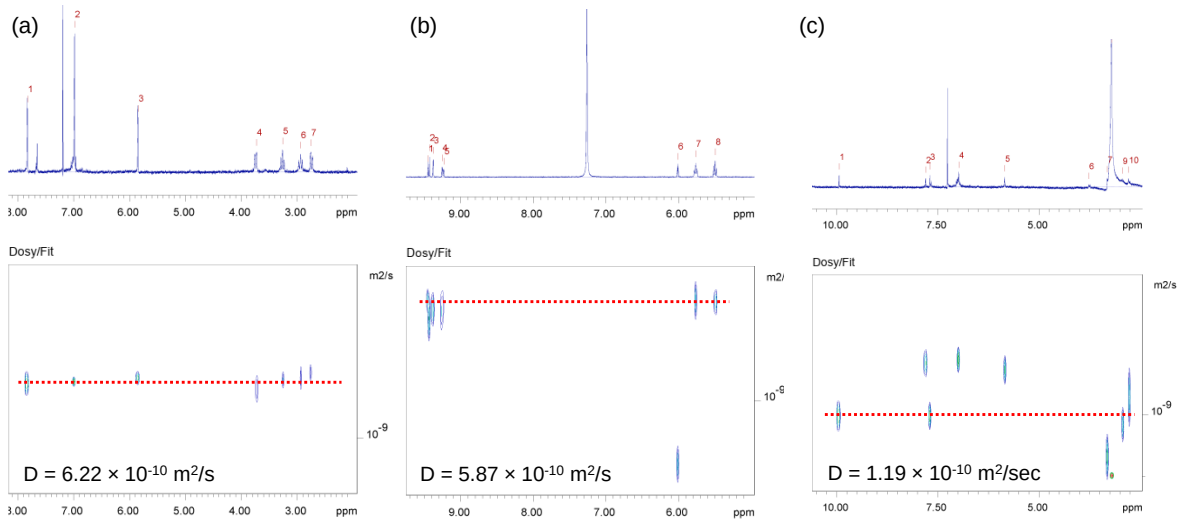


Fig. S24. ^{1}H-^{1}H DOSY spectrum of (a) **4** (5 mM), (b) dopamine (33 mM) and (c) a mixture of **4** (5 mM) and dopamine (33 mM) in 50% $CDCl_3$-CH_3OD.

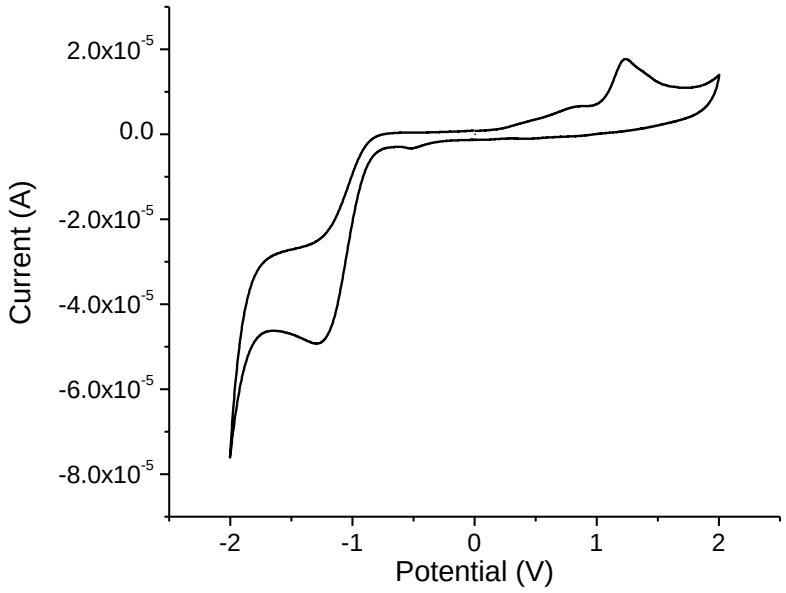


Fig. S25. Cyclic voltammogram of the molecular capsule **4** (1 mM) in chloroform using 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte at a scanning rate of 50 mV/s.

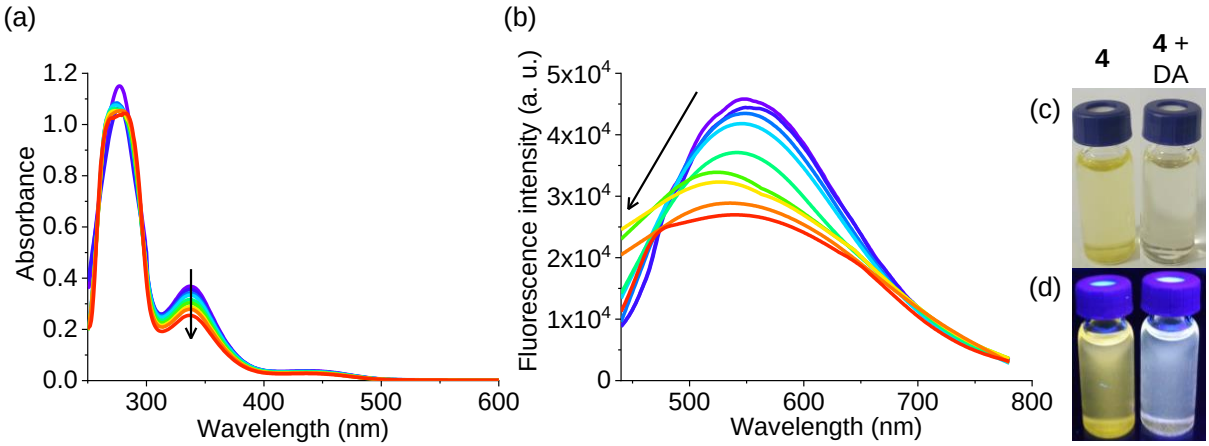


Fig. S26. (a) Changes in the absorption and (b) emission spectrum of **4** (10 μM) with the addition of dopamine (0–100 μM) in DMSO. Photographs of a solution of **4** (10 μM) in the presence of dopamine (100 μM) in DMSO under (c) ambient and (d) UV light.

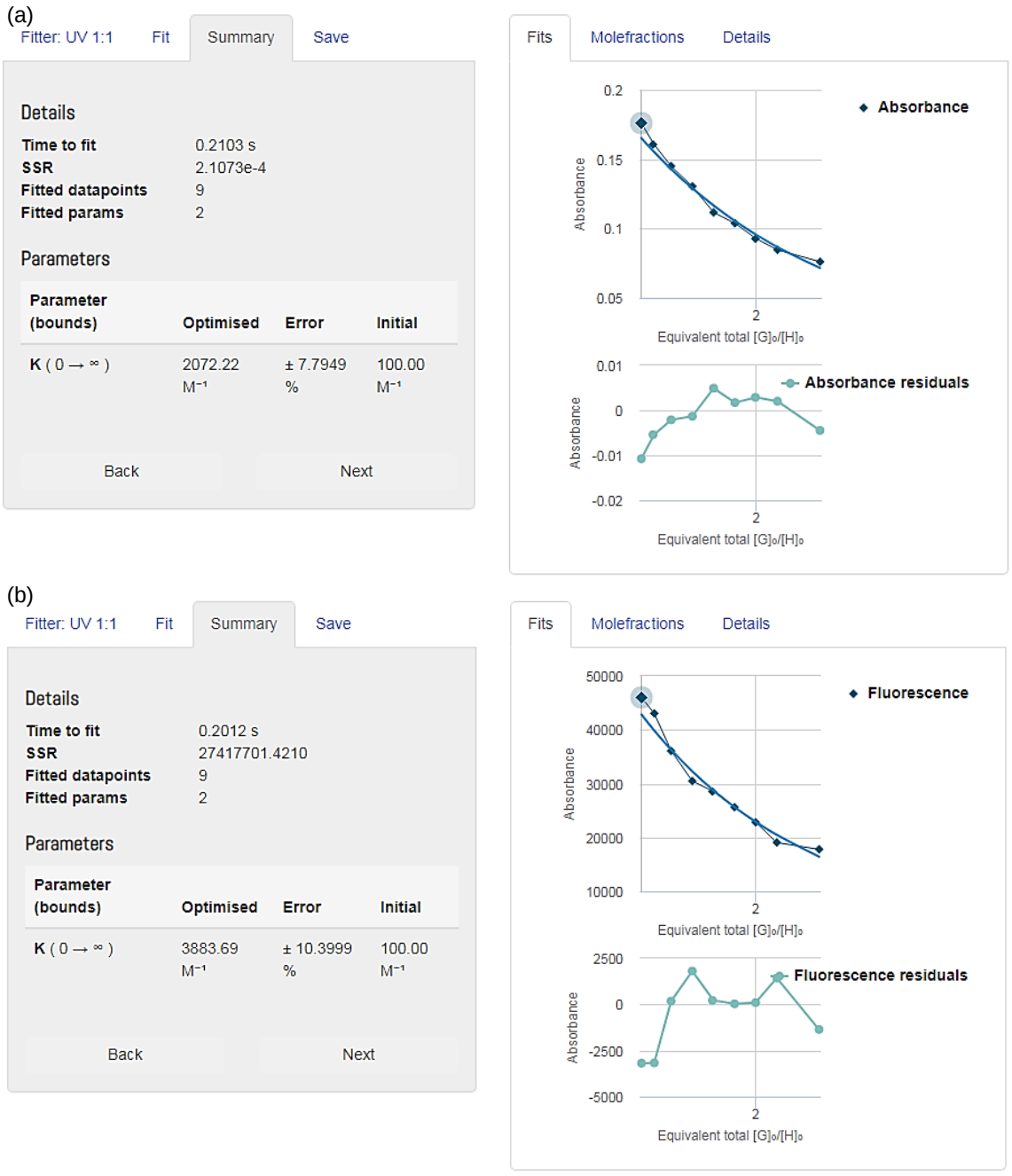


Fig. S27. Screenshots taken from the summary window of the website supramolecular.org. This screenshots shows the raw data for titration of **4** with dopamine in DMSO and the data fitted to 1:1 binding model using (a) absorption and (b) emission titration data.

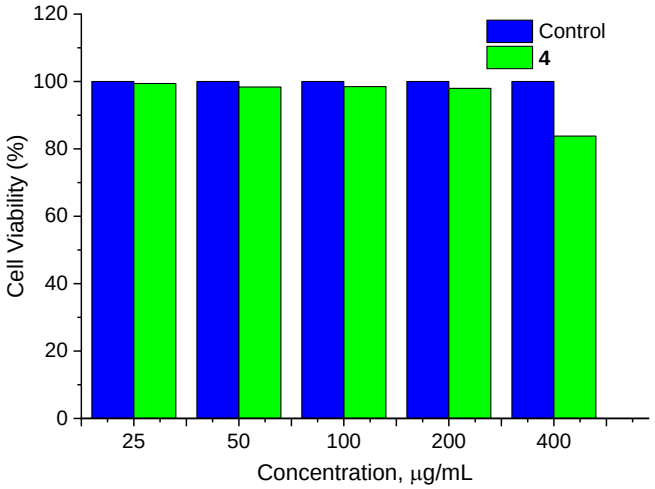


Fig. S28. Dose-dependent biocompatibility of the molecular capsule **4** with SHSY cells.

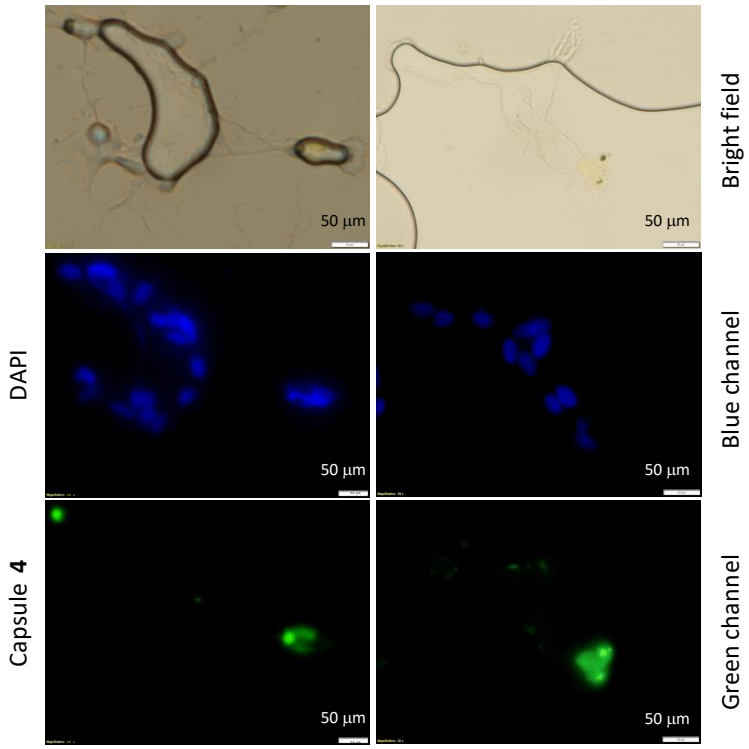


Fig. S29. Fluorescence microscope images of SHSY neuron cells treated with capsule **4** and DAPI.