

Supporting Information

Recognition of nitrotoluenes with bowl-shaped Tröger's base derivatives

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1. Fluorescence titration of *calix-1* with analytes.

Fluorescence studies. Steady-state fluorescence measurements were recorded on an Edinburgh Instrument Fluorimeter (FLS920) equipped with a Xe-lamp (Osram XBO450W) and a single-photon counting PMT (Hamamatsu R955). Quantum yield measurements were obtained with a Hamamatsu Quantaurus-QY (C11347-11) absolute quantum yield automated integrating sphere. Solutions of the sensors in spectrophotometric grade CH_2Cl_2 or ethanol (CH_2Cl_2 was filtered through a basic alumina cartridge prior to every use) were prepared from concentrated stock solutions and adjusted to $A < 0.1$ units. Analyte solutions were prepared in solutions of sensors at the same concentration used in the experiments to compensate for dilution. 1 cm optical-path cells were used for all the experiments.

Figure S1. Titration of *calix-1* (5.0×10^{-6} M) in CH_2Cl_2 with a solution of 2,4-DNT in the same solvent. *Left panel:* overlaid spectra recorded over the course of the titration ($\lambda_{\text{exc}} = 332$ nm). *Right panel:* normalized response isotherm at a selected wavelength. *Bottom panel:* linear plot for the determination of quenching constant.

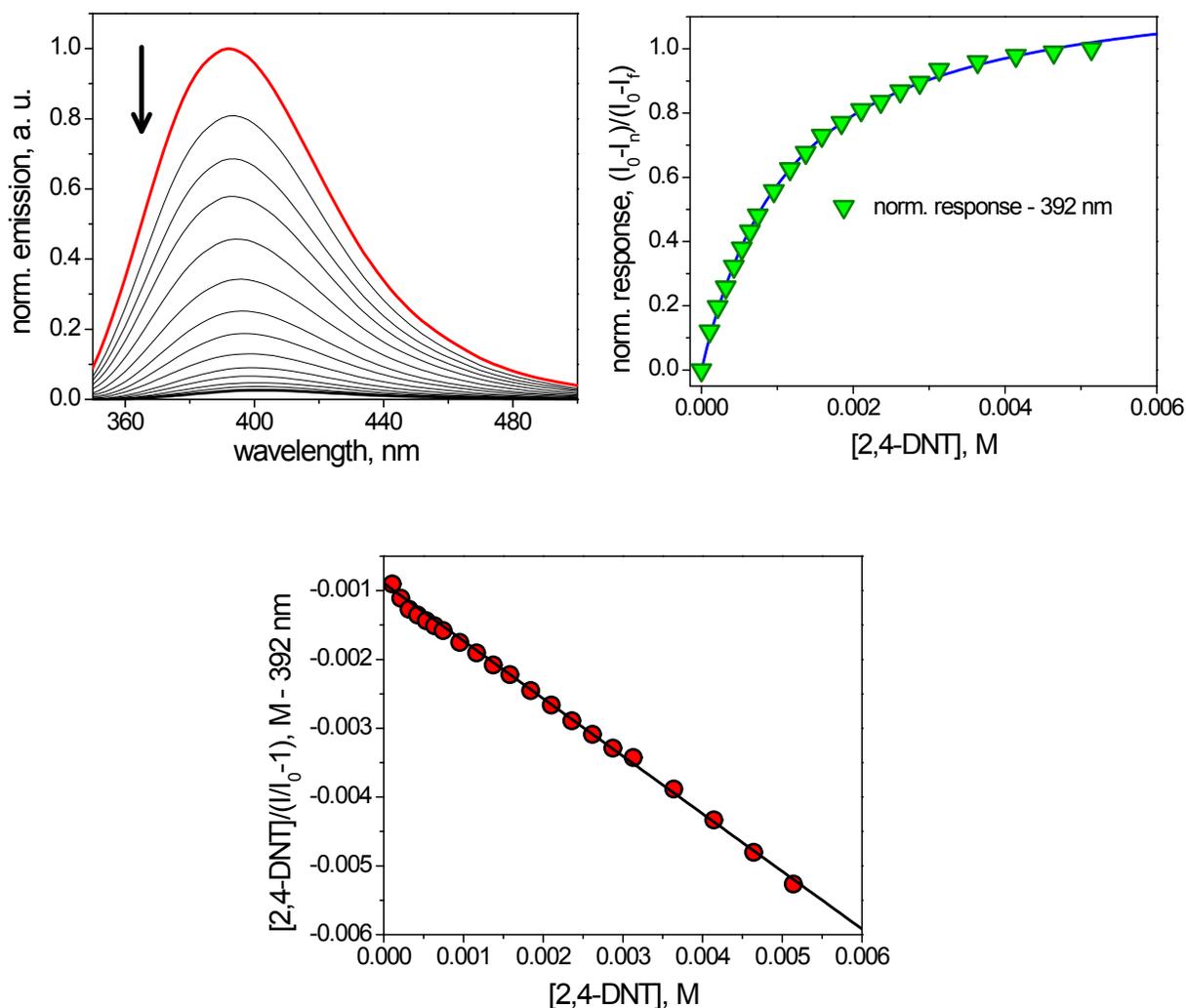


Figure S2. Titration of *calix-1* (5.0×10^{-6} M) in EtOH with a solution of 2,4-DNT in the same solvent. *Left panel:* overlaid spectra recorded over the course of the titration ($\lambda_{\text{exc}} = 332$ nm). *Right panel:* normalized response isotherm at a selected wavelength. *Bottom panel:* linear plot for the determination of quenching constant.

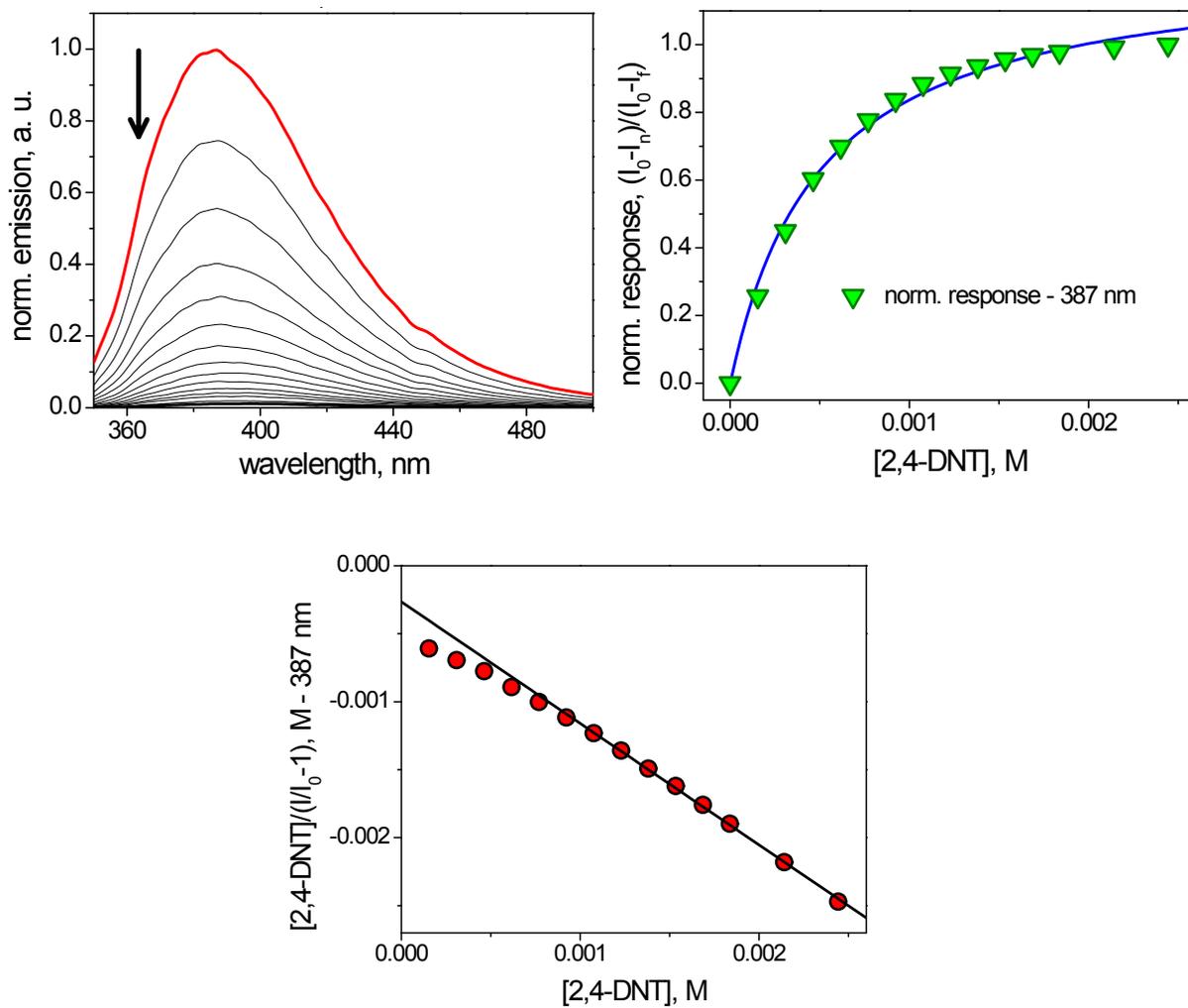


Figure S3. Titration of *calix-1* (5.0×10^{-6} M) in CH_2Cl_2 with a solution of 2,6-DNT in the same solvent. *Left panel:* overlaid spectra recorded over the course of the titration ($\lambda_{\text{exc}} = 332$ nm). *Right panel:* normalized response isotherm at a selected wavelength. *Bottom panel:* linear plot for the determination of quenching constant.

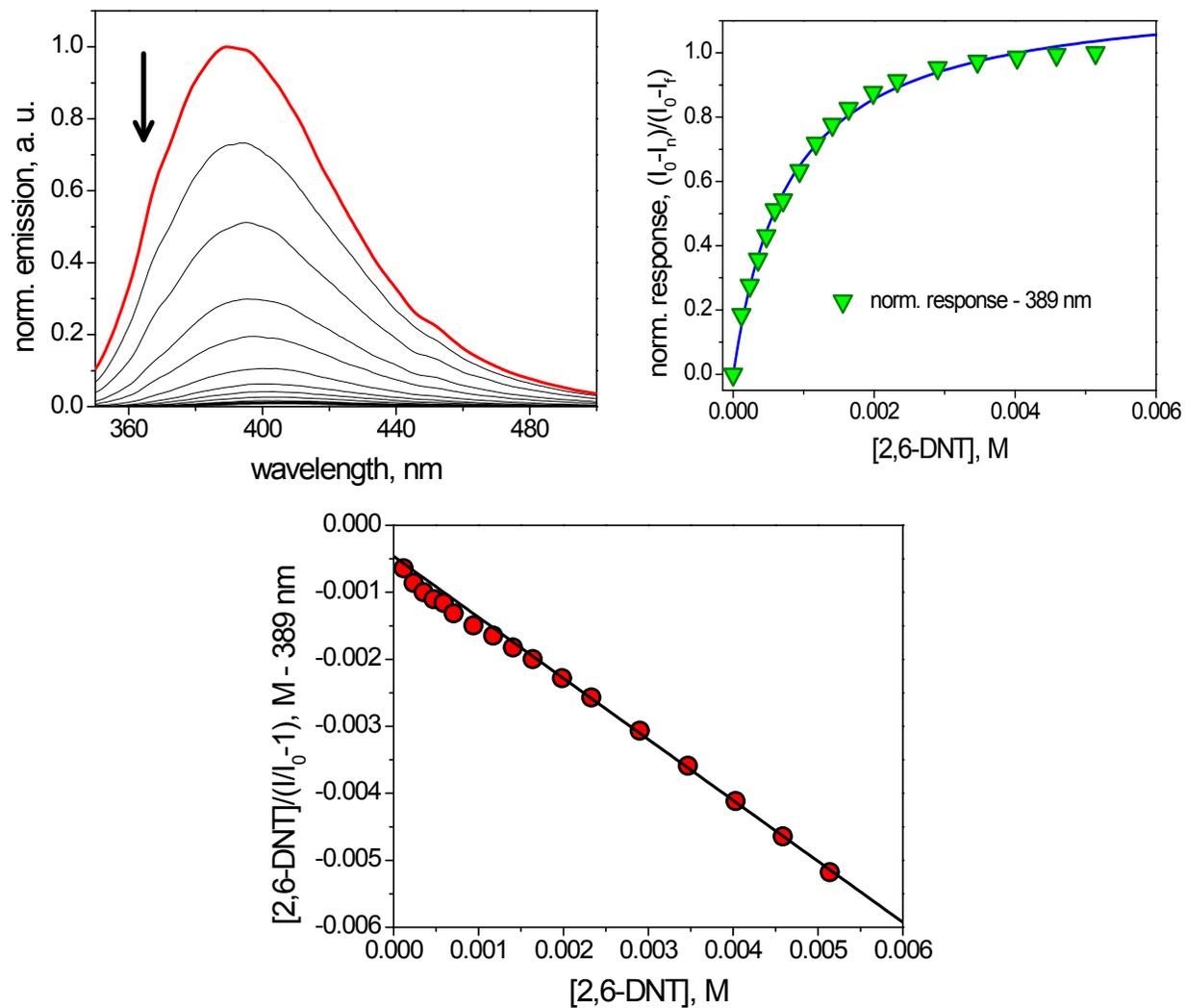


Figure S4. Titration of *calix-1* (5.0×10^{-6} M) in EtOH with a solution of 2,6-DNT in the same solvent. *Left panel:* overlaid spectra recorded over the course of the titration ($\lambda_{\text{exc}} = 332$ nm). *Right panel:* normalized response isotherm at a selected wavelength. *Bottom panel:* linear plot for the determination of quenching constant.

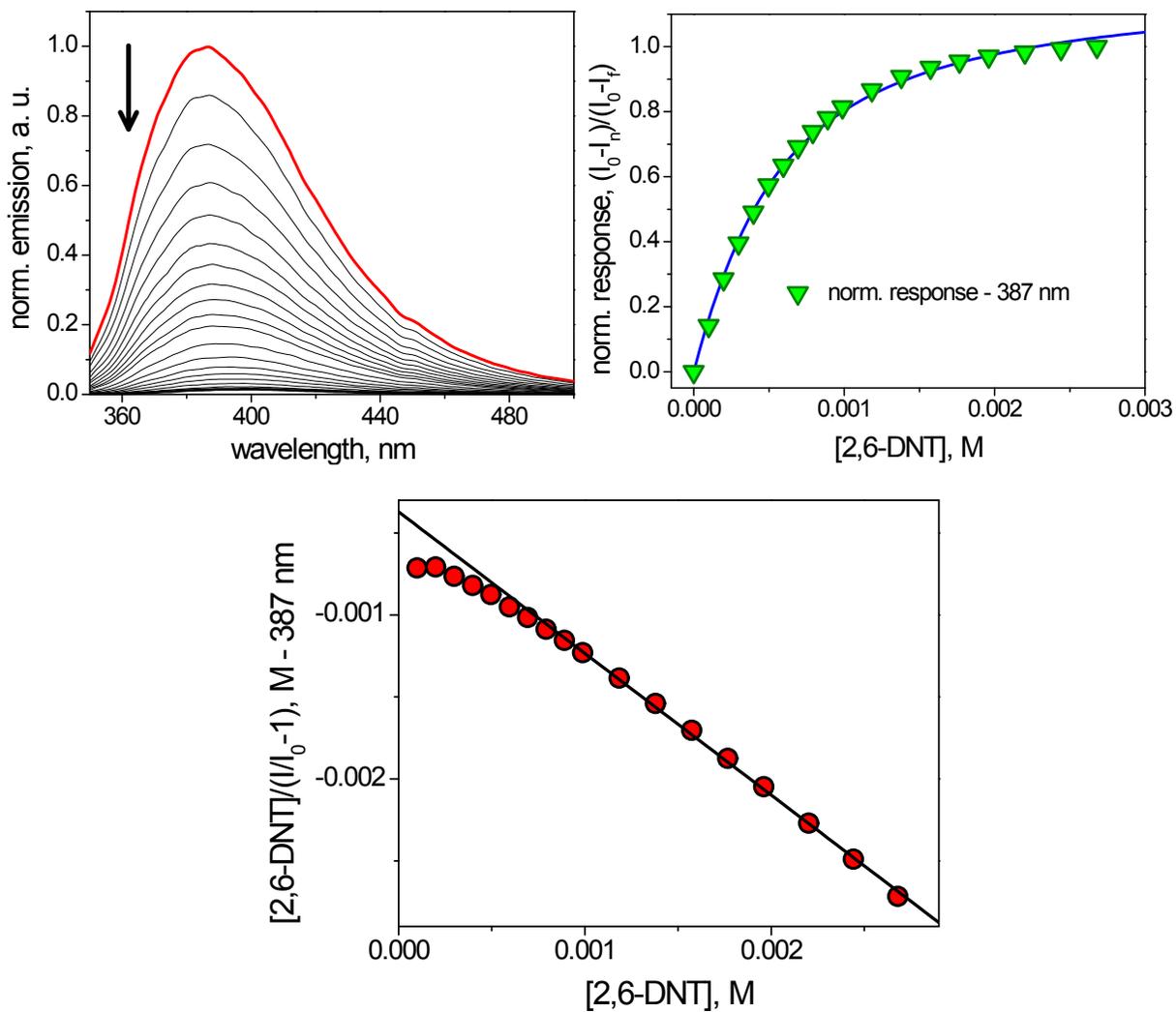


Figure S5. Titration of *calix-1* (5.0×10^{-6} M) in CH_2Cl_2 with a solution of DMDNB in the same solvent. *Top panel:* overlaid spectra recorded over the course of the titration ($\lambda_{\text{exc}} = 332$ nm). *Bottom panel left:* normalized response isotherm at a selected wavelength. *Bottom panel:* linear plot for the determination of quenching constant.

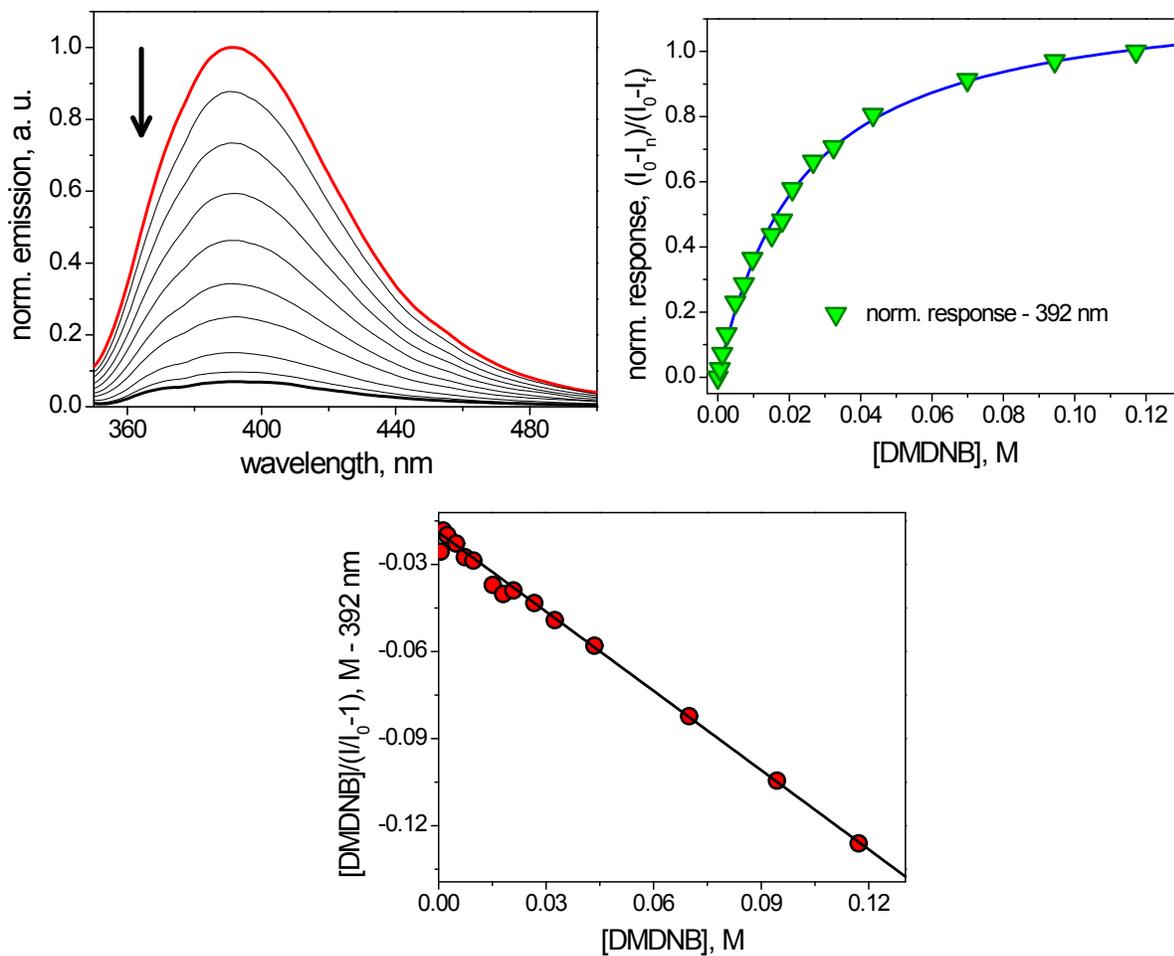


Figure S6. Titration of *calix-1* (5.0×10^{-6} M) in CH_2Cl_2 with a solution of TNT in the same solvent. *Left panel:* overlaid spectra recorded over the course of the titration ($\lambda_{\text{exc}} = 332$ nm). *Right panel:* normalized response isotherm at a selected wavelength. *Bottom panel:* linear plot for the determination of quenching constant.

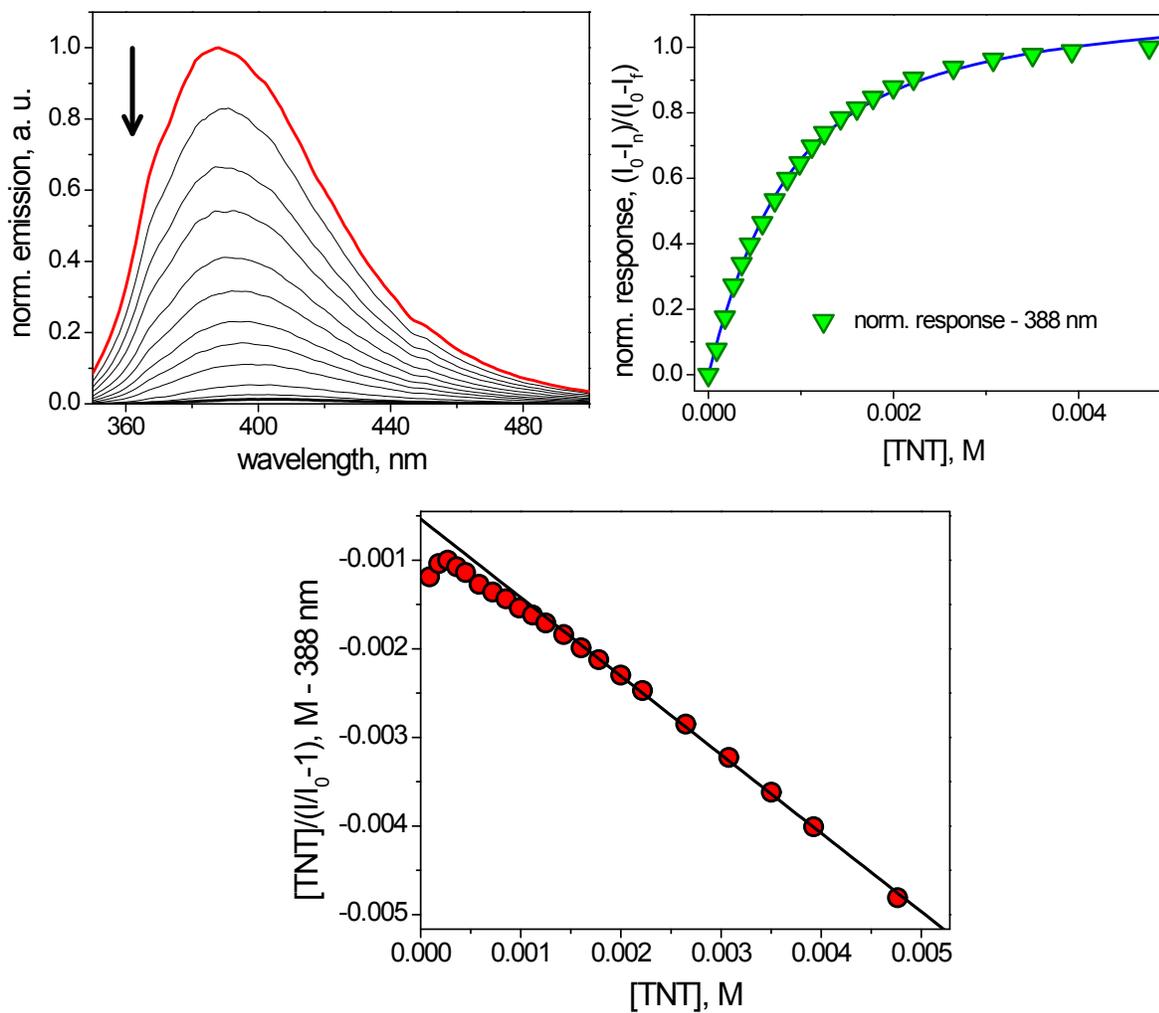
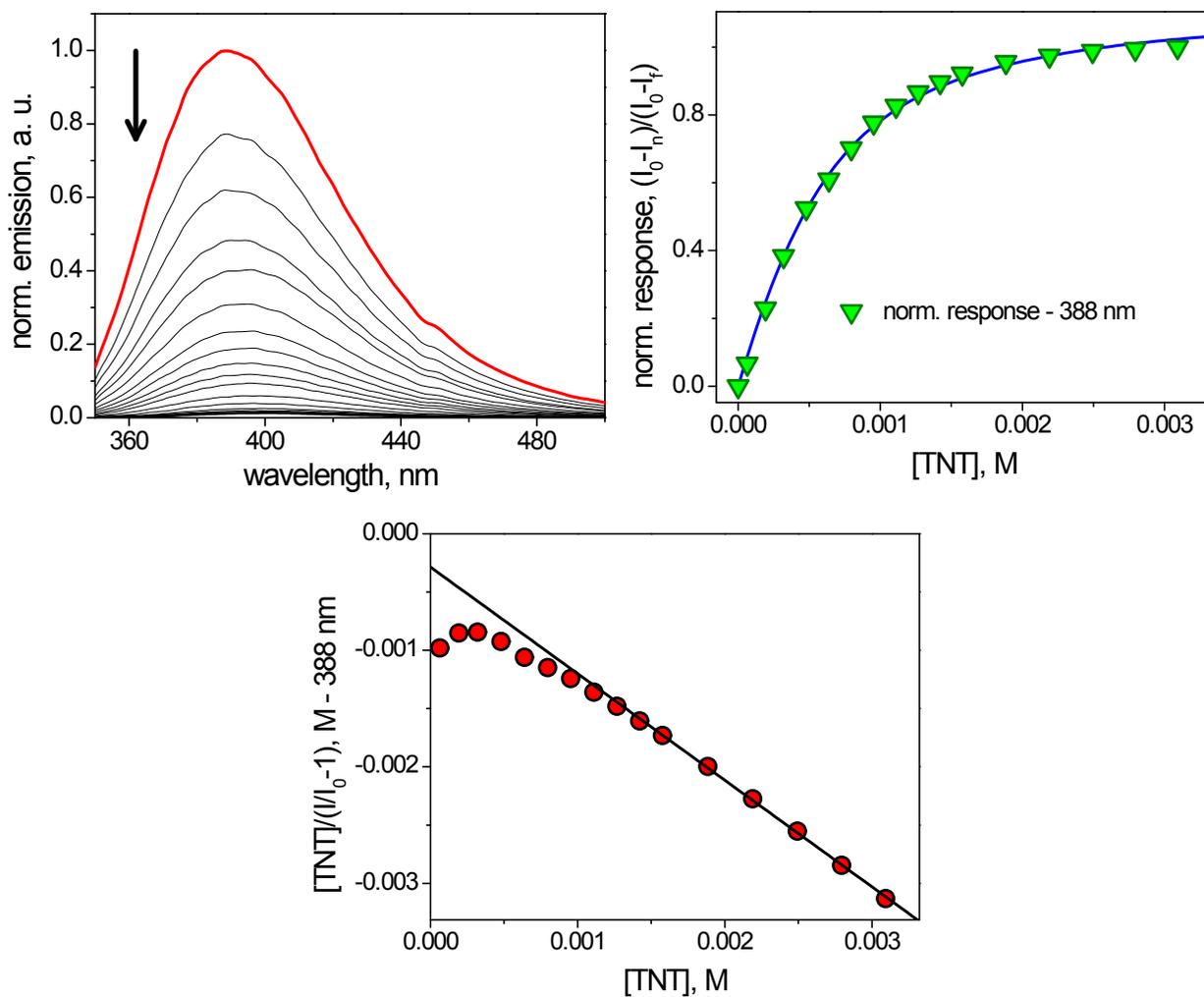


Figure S7. Titration of *calix-1* (5.0×10^{-6} M) in EtOH with a solution of TNT in the same solvent. *Left panel:* overlaid spectra recorded over the course of the titration ($\lambda_{\text{exc}} = 332$ nm). *Right panel:* normalized response isotherm at a selected wavelength. *Bottom panel:* linear plot for the determination of quenching constant.



2. Fluorescence titration of *calix-2* with analytes.

Figure S8. Titration of *calix-2* (5.0×10^{-6} M) in CH_2Cl_2 with a solution of 2,4-DNT in the same solvent. *Left panel:* overlaid spectra recorded over the course of the titration ($\lambda_{\text{exc}} = 335$ nm). *Right panel:* normalized response isotherm at a selected wavelength. *Bottom panel:* linear plot for the determination of quenching constant.

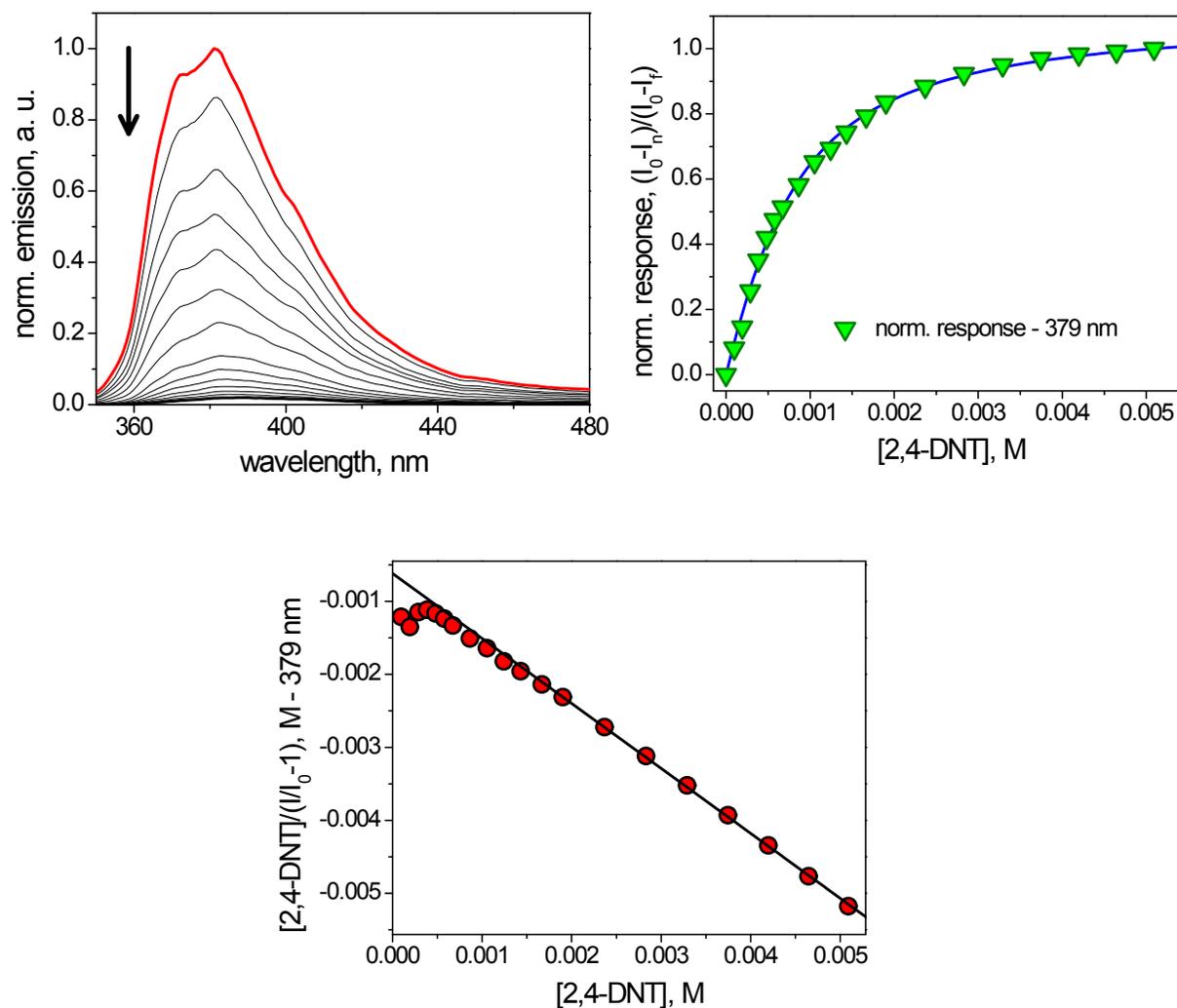


Figure S9. Titration of *calix-2* (5.0×10^{-6} M) in EtOH with a solution of 2,4-DNT in the same solvent. *Left panel:* overlaid spectra recorded over the course of the titration ($\lambda_{\text{exc}} = 335$ nm). *Right panel:* normalized response isotherm at a selected wavelength. *Bottom panel:* linear plot for the determination of quenching constant.

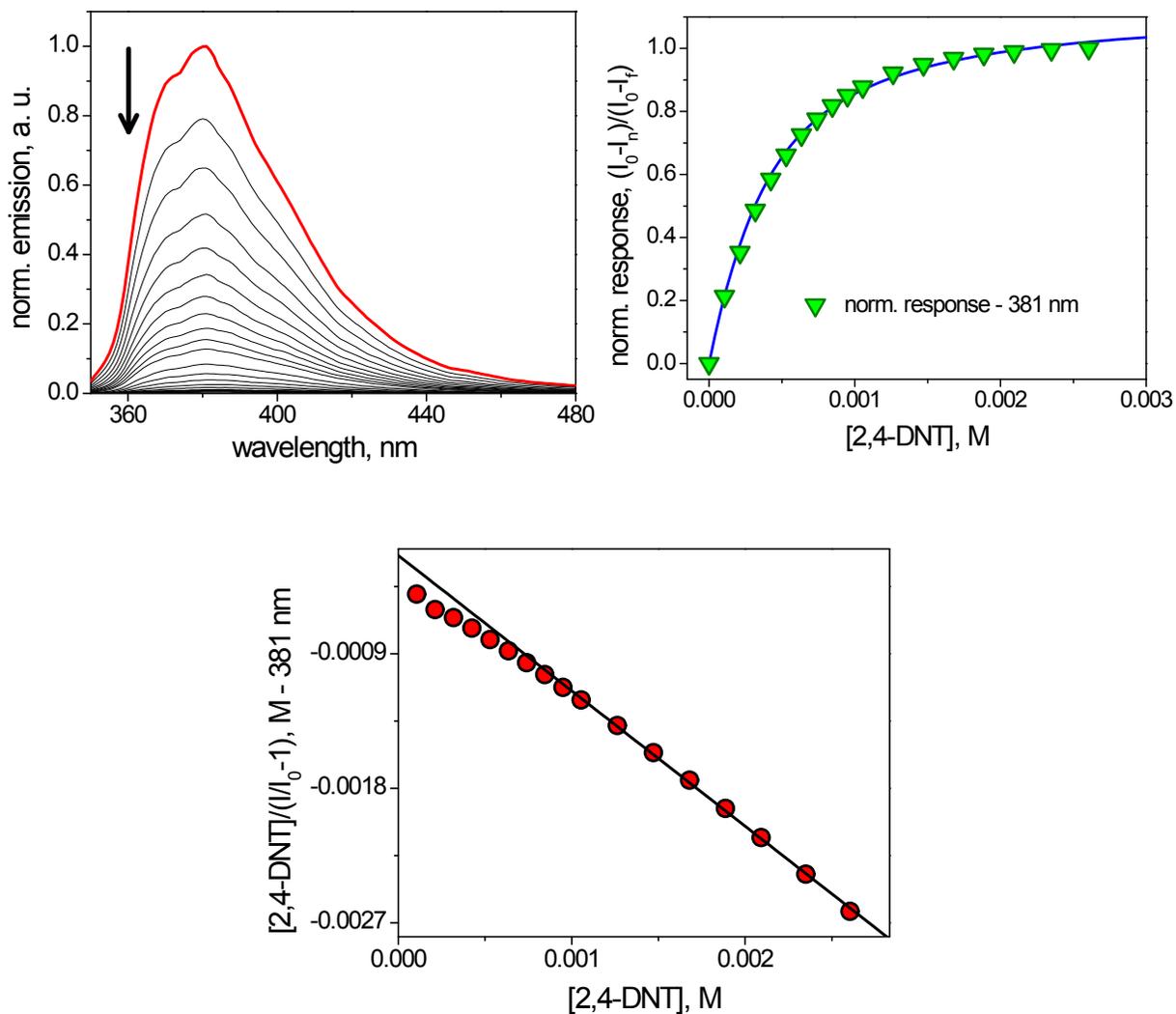


Figure S10. Titration of *calix-2* (5.0×10^{-6} M) in CH_2Cl_2 with a solution of 2,6-DNT in the same solvent. *Left panel:* overlaid spectra recorded over the course of the titration ($\lambda_{\text{exc}} = 335$ nm). *Right panel:* normalized response isotherm at a selected wavelength. *Bottom panel:* linear plot for the determination of quenching constant.

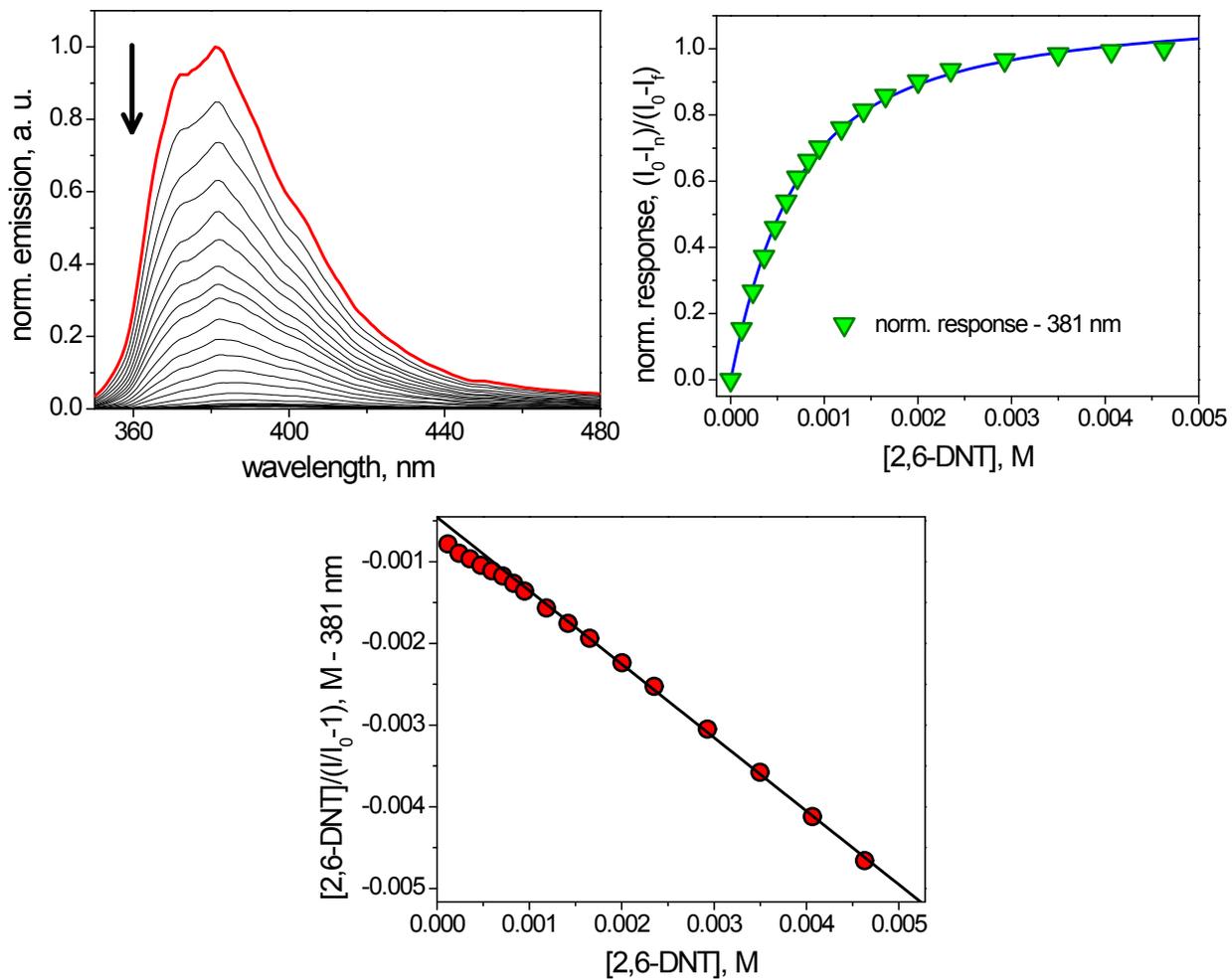


Figure S11. Titration of *calix-2* (5.0×10^{-6} M) in EtOH with a solution of 2,6-DNT in the same solvent. *Left panel:* overlaid spectra recorded over the course of the titration ($\lambda_{\text{exc}} = 335$ nm). *Right panel:* normalized response isotherm at a selected wavelength. *Bottom panel:* linear plot for the determination of quenching constant.

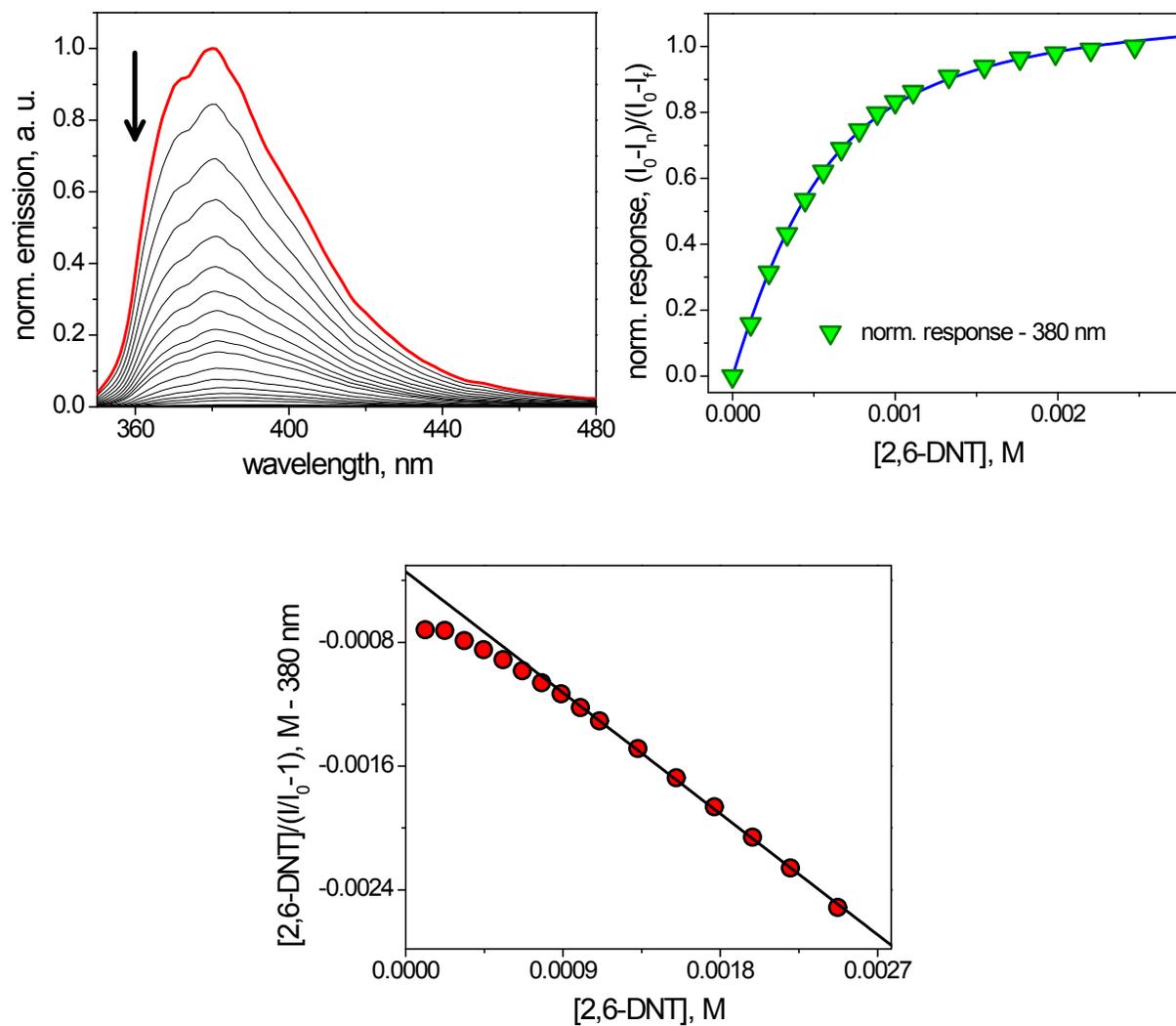


Figure S12. Titration of *calix-2* (5.0×10^{-6} M) in CH_2Cl_2 with a solution of DMDNB in the same solvent. *Top panel:* overlaid spectra recorded over the course of the titration ($\lambda_{\text{exc}} = 335$ nm). *Bottom panel left:* normalized response isotherm at a selected wavelength. *Bottom panel:* linear plot for the determination of quenching constant.

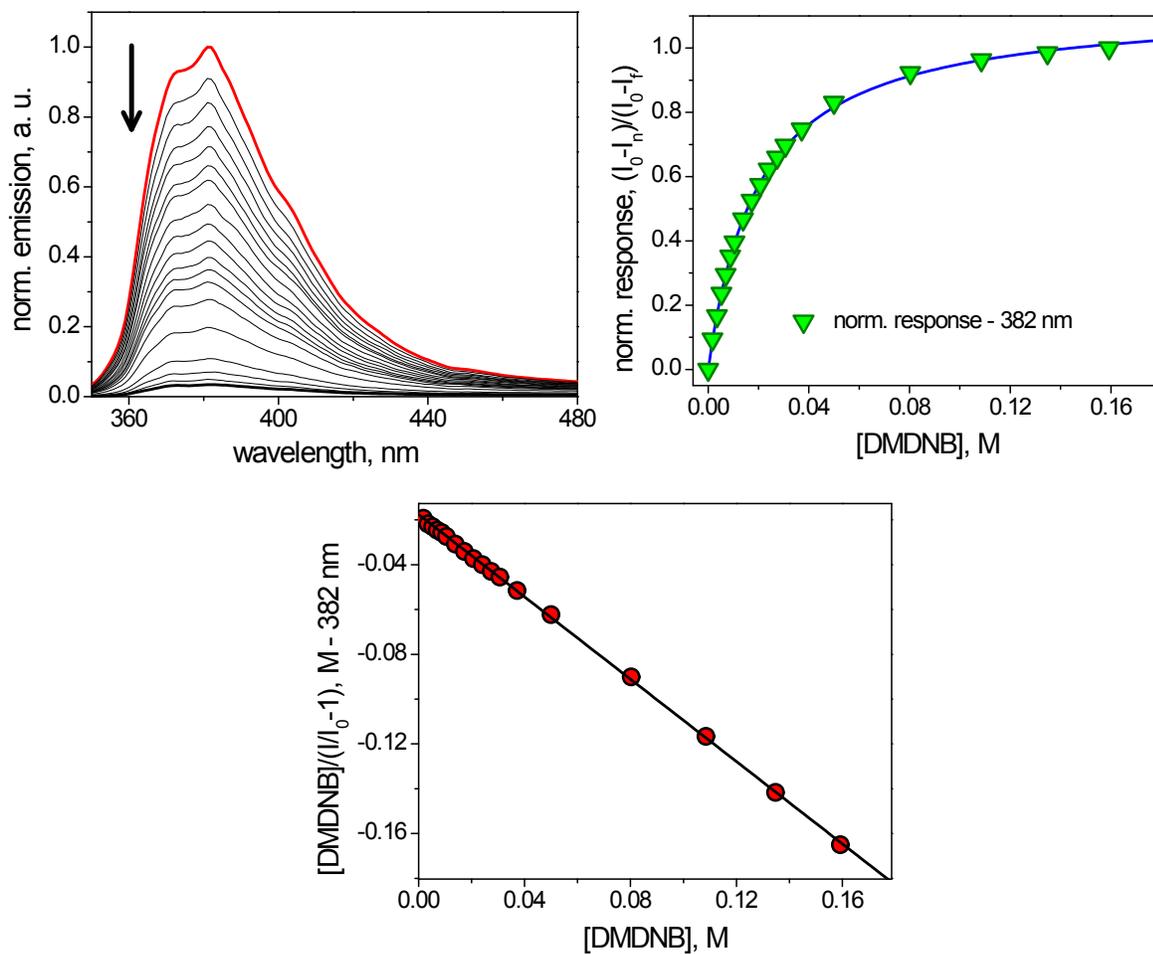
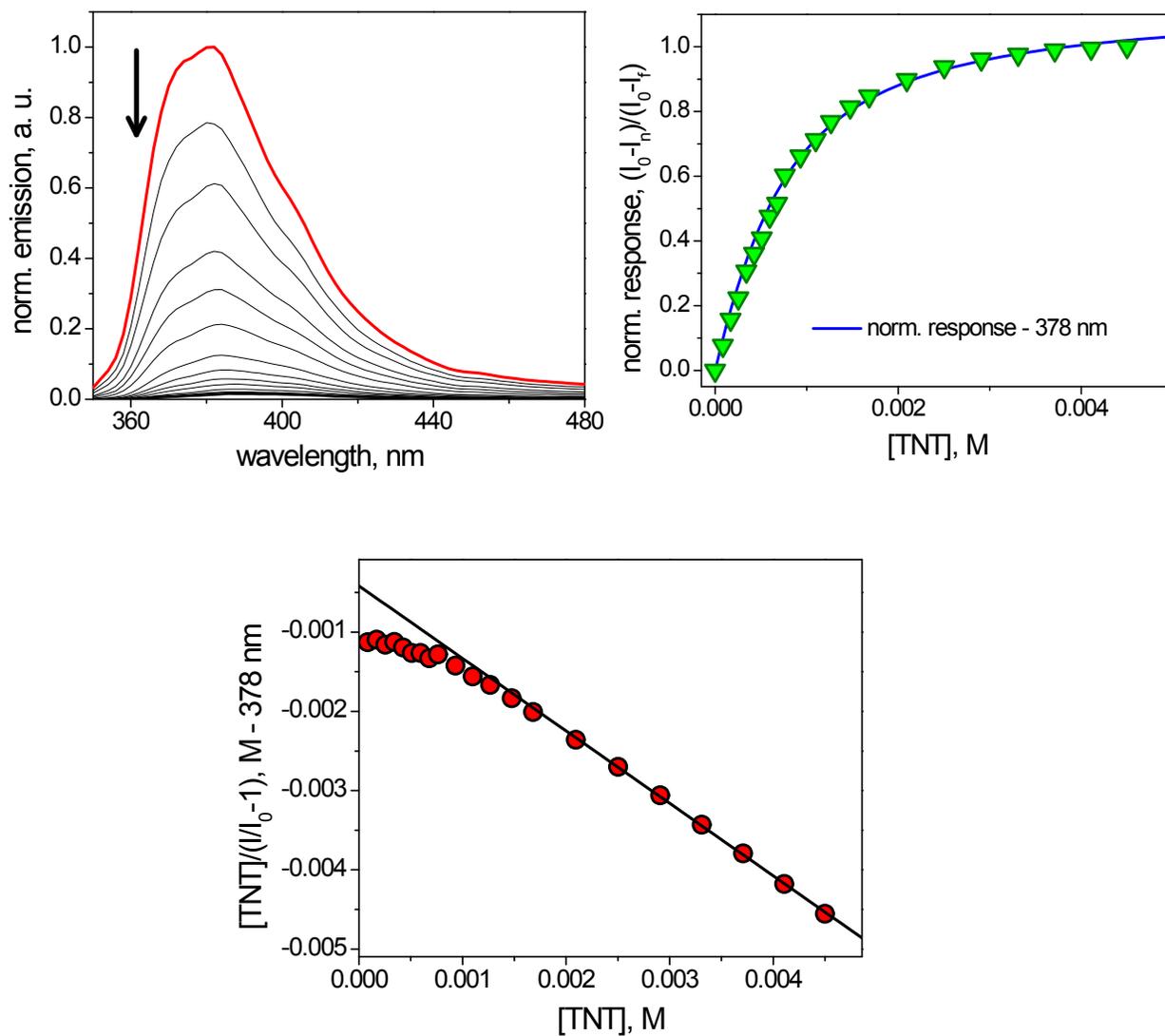


Figure S13. Titration of *calix-2* (5.0×10^{-6} M) in CH_2Cl_2 with a solution of TNT in the same solvent. *Left panel:* overlaid spectra recorded over the course of the titration ($\lambda_{\text{exc}} = 335$ nm). *Right panel:* normalized response isotherm at a selected wavelength. *Bottom panel:* linear plot for the determination of quenching constant.



3. Single crystal diffraction studies.

Crystallographic experimental details. Depending on the diffraction power of the single crystals and size of the unit cell, the data were collected on a Bruker D8 VENTURE system equipped with a multilayer monochromator and a Mo $K\alpha$ Incoatec microfocus sealed tube, $\lambda = 0.71073 \text{ \AA}$ (*calix-1*•NB) and Cu $K\alpha$ Incoatec microfocus sealed tube, $\lambda = 1.54184 \text{ \AA}$ (*calix-2*•2NB) using combined φ - and ω -scans at 180 K. The frames were integrated with the Bruker SAINT¹ software package using a wide-frame algorithm. Data were corrected for absorption effects using the Multi-Scan method (SADABS²). *Calix-1*•CH₂Cl₂ data were collected on an Oxford Xcalibur PX, Cu $K\alpha$ ENHANCED sealed tube, $\lambda = 1.54184 \text{ \AA}$ using ω -scans at 190 K. Data were corrected for absorption effects using the Multi-Scan method (CrysAlisPro³). The positional and anisotropic thermal parameters of all non-hydrogen atoms were refined. All H atoms were located in a difference map, but repositioned geometrically, then they were initially refined with soft restraints on the bond lengths and angles to regularise their geometry (C–H in the range of 0.93-0.98 \AA) and $U_{iso}(\text{H})$ (in the range 1.2-1.5 times U_{eq} of the parent atom), after which the positions of carbon bound hydrogen atoms were refined with riding constraints. *Calix-1*•NB: planarity, distance and DELU, SIMU restraints were used to improve geometry of nitrobenzene. *Calix-2*•2NB: DELU, SIMU restraints were used to correct ADP's on one nitrobenzene. *Calix-1*•CH₂Cl₂: distance restraints were used to regularize the geometry of dichloromethane molecules. Fractional occupancy was refined to describe the disorder in one molecule of dichloromethane. Data collection: APEX3 v2015,⁴ CrysAlisPro CCD;³ unit cell refinement: APEX3 v2015,⁴ CrysAlisPro RED; data reduction: SAINT,¹ CrysAlisPro RED; program used to solve structure: SIR92;⁵ program used to refine structure: CRYSTALS.⁶

Table S1. Crystal data for *calix-1*•NB, *calix-1*•CH₂Cl₂, and *calix-2*•2NB.

	<i>calix-1</i> •NB	<i>calix-1</i> •CH ₂ Cl ₂	<i>calix-2</i> •2NB
CCDC No.	1485246	1485248	1485247
formula	C ₄₅ H ₃₆ N ₆ , C ₆ H ₅ NO ₂	C ₄₅ H ₃₆ N ₆ , CH ₂ Cl ₂	C ₅₇ H ₄₂ N ₆ , 2(C ₆ H ₅ NO ₂)
formula weight	783.93	745.75	1057.19
crystal description	plate	needle	plate
crystal color	green	orange	green
dimensions (mm)	0.111 \times 0.168 \times 0.272	0.087 \times 0.159 \times 0.549	0.030 \times 0.110 \times 0.160
ρ_{calc} (g cm ⁻³)	1.377	1.351	1.361
crystal system	monoclinic	triclinic	monoclinic
radiation type	Mo K α	Cu K α	Cu K α
wavelength (Å)	0.71073	1.54180	1.54180
<i>a</i> (Å)	11.998(6)	17.9422(14)	21.3761(8)
<i>b</i> (Å)	14.423(6)	18.3629(16)	12.4047(4)
<i>c</i> (Å)	21.871(9)	20.9128(13)	21.2424(7)
α (°)	90	107.088(7)	90
β (°)	92.101(16)	100.483(6)	113.697(2)
γ (°)	90	116.305(8)	90
<i>V</i> (Å ³)	3782.1(15)	5498.3(3)	5157.79(17)
<i>T</i> (K)	180	180	180
space group	P 1 21/c 1	P -1	P 2 ₁ /c 1 1
<i>Z</i>	4	6	4
μ (mm ⁻¹)	0.086	1.929	0.685
θ range (°)	1.864–25.349	4.404–73.510	4.185–68.396
reflns collected	54809	22877	54859
independent reflns	6930	22877	9440
scan type	ω -scans	φ - and ω -scans	φ - and ω -scans
<i>R</i> _{int}	0.108	0.102	0.148
strong data (<i>I</i> > 2 σ (<i>I</i>))	4025	11270	5383
<i>RI</i> , <i>wR</i> (<i>F</i> ²) (<i>I</i> > 2 σ (<i>I</i>))	0.1093, 0.2715	0.0951, 0.1854	0.0931, 0.2275
<i>RI</i> , <i>wR</i> (<i>F</i> ²) (all data)	0.1721, 0.3448	0.1475, 0.2526	0.1467, 0.2669
GOF on <i>F</i> ²	1.0686	1.0114	1.0109
Δr_{max} , Δr_{min} (e Å ⁻³)	1.56, -1.06	1.39, -1.81	0.51, -0.58

Figure S14. Structure of *calix-1*•NB. Thermal ellipsoids were scaled to a 50% probability. The nitrobenzene molecule is shaded in purple hues.

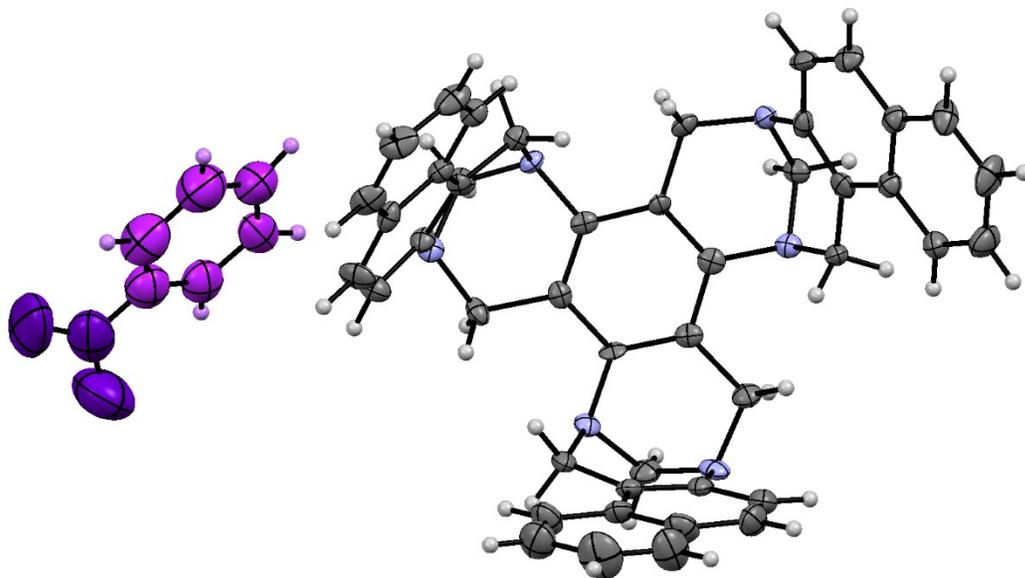


Figure S15. Structure of *calix-1*•NB. Thermal ellipsoids were scaled to a 50% probability. The nitrobenzene molecule is shaded in purple hues.

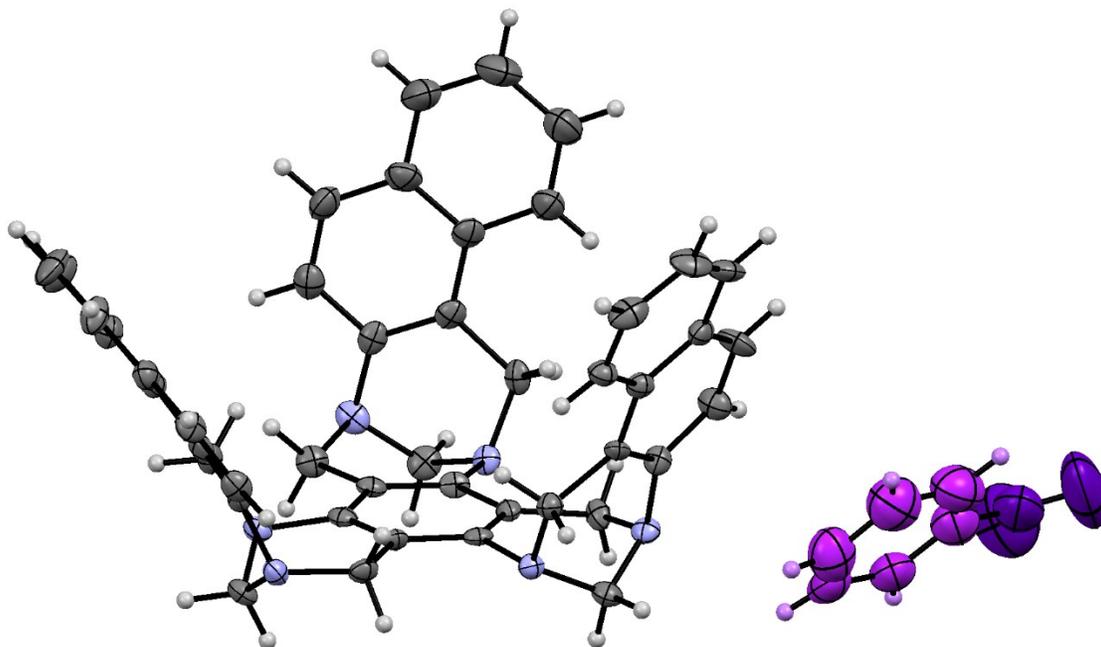


Figure S16. Structure of *calix-1*•NB. *Left:* thermal ellipsoids were scaled to a 50% probability. (*Right:* space fill model. Two interpenetrating *calix-1* molecule are represented here in red and blue color, respectively. The nitrobenzene molecule was removed for clarity.

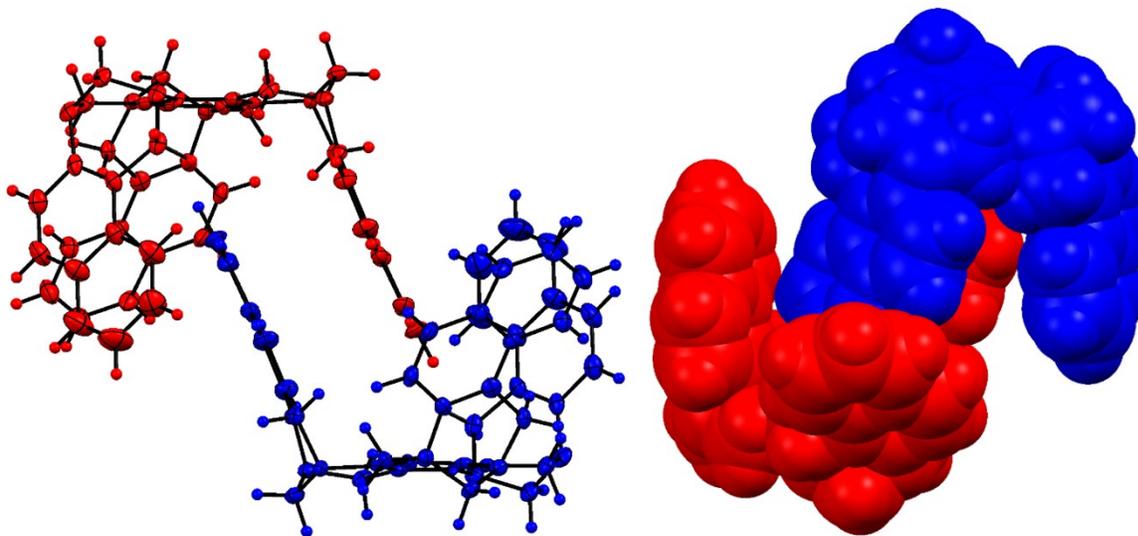
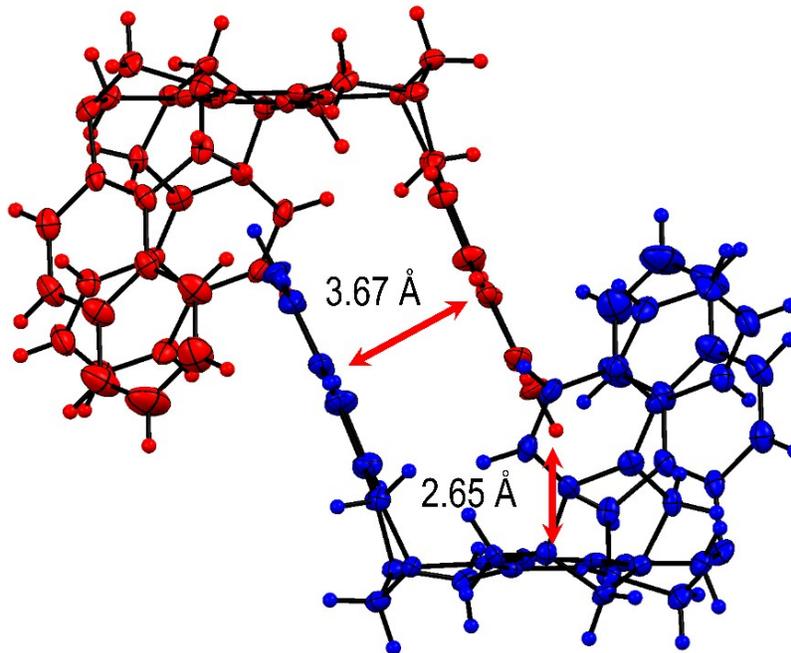


Figure S17. Distances measured on *calix-1* between the two naphthalene moieties and between the naphthalene and the triphenylene moieties.

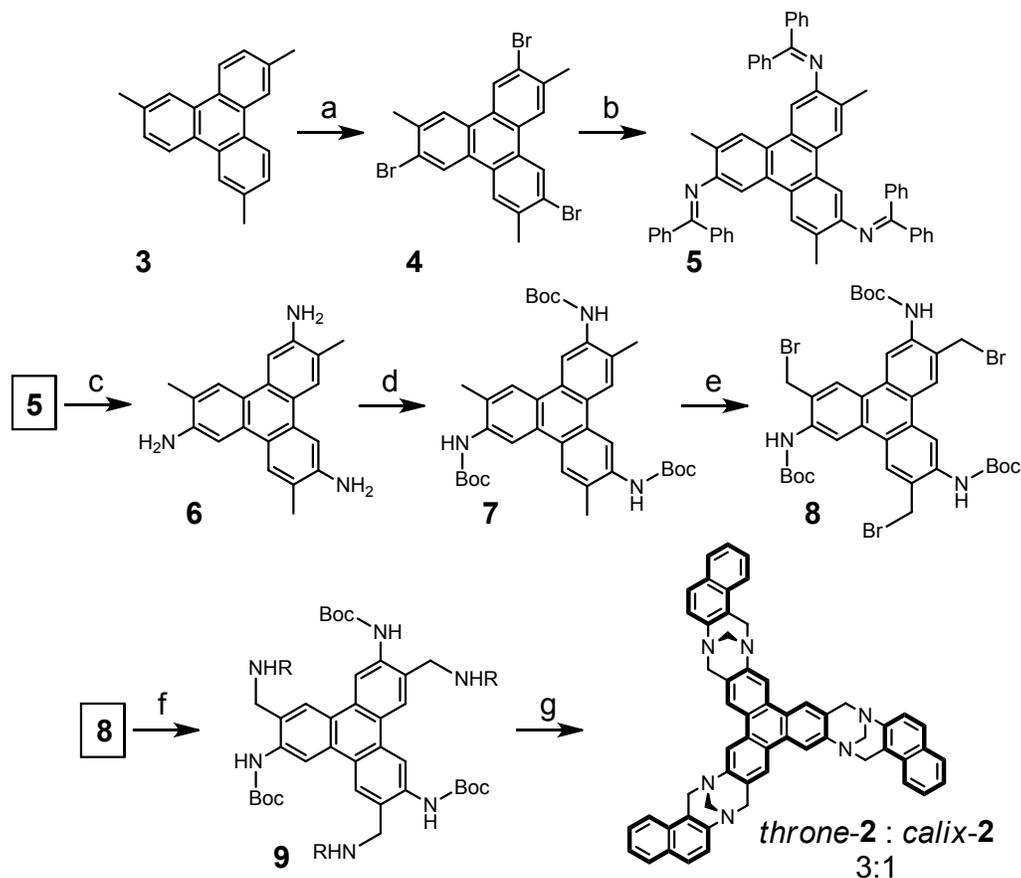


4. Experimental details and syntheses.

General Methods. All chemicals were purchased from commercial suppliers and were used without further purification. 2,6,10-trimethyltriphenylene (**3**) was synthesized according to a published procedure.⁷ NMR spectra were recorded with a 300 MHz or 500 MHz instrument at room temperature (ca. 22 °C) in CDCl₃ or [D₆]DMSO. The chemical shifts (δ) are presented in ppm, and coupling constants (J) are in Hz. Mass spectra were obtained using electrospray ionisation (ESI) with a LTQ Orbitrap spectrometer. Silica (32-63 μm , 60 Å) was used to purify the products by column chromatography.

Synthesis of calix-2. Calix-2 was prepared as follows: 2,6,10-trimethyltriphenylene (**3**)⁷ was brominated with bromine in presence of iron in nitrobenzene to afford tribromide **4** in 77% yield.⁸ The amino-group was introduced via the palladium-catalysed imination to **5**,⁹ followed by acidic hydrolysis to obtain the final triamine **6** in an overall yield of 80%. The more straightforward synthetic route to compound **6** via the direct nitration of the triphenylene ring, followed by reduction, has been attempted without success. The triamine **6** was then reacted with di-tert-butyl dicarbonate (Boc₂O) in tetrahydrofuran to afford the protected triamine **7** in 97% yield. This was followed by the radical bromination with *N*-bromosuccinimide (NBS) and 2,2'-azobis(2-methylpropionitrile) (AIBN) using an infrared lamp (250 W) to give tribromide **8** in 73% yield. The nucleophilic substitution of the bromide with 2-aminonaphthalene gave hexamine **9** in 86% yield. The final treatment of **9** with paraformaldehyde in trifluoroacetic acid (TFA) provided the tris-Tröger product **2** in 76% yield as a mixture of two diastereomers: *throne-2* (58%) and *calix-2* (18%) in a 3:1 ratio.

Scheme S1. Synthetic pathway to *calix-2*. a) Br₂, Fe, PhNO₂, 110 °C, overnight, 77%; b) Ph₂C=NH, Pd₂(dba)₃, *rac*-BINAP, *t*BuONa, PhMe, 110 °C, 24h, 91%; c) HCl aq., THF, rt, 2h, 88%; d) Boc₂O, THF, reflux, overnight, 97%; e) NBS, AIBN, 250W IR-lamp, CCl₄, 5h, 73%; f) 2-aminonaphthalene, DMF, 50 °C, 5h, 86%; g) (CH₂O)_n, TFA, rt, overnight, 76%.



2,6,10-tribromo-3,7,11-trimethyltriphenylene (4): 4 was prepared by a modification of an existing procedure.⁸ To a mixture of 2,6,10-trimethyltriphenylene (**3**) (2.7 g, 9.99 mmol) and iron (0.1 g, 1.8 mmol) in nitrobenzene (50 mL) was added bromine (2.1 mL, 6.4 g, 40.0 mmol). The reaction mixture was heated at 100 °C overnight. Diethylether (150 mL) was added after cooling to room temperature and the precipitated solid was filtered off, washed with diethylether and dried in *vacuo*. Tribromide **4** (3.9 g, 7.69 mmol, 77 %) was obtained by recrystallization from bromobenzene. Characterization of **4** matches the data reported in the existing literature.⁸

***N*²,*N*⁶,*N*¹⁰-tris(diphenylmethylene)-3,7,11-trimethyltriphenyl-ene-2,6,10-triamine (5):** A mixture of tribromide **4** (2.0 g, 3.94 mmol), tris(dibenzylidenacetone) dipalladium(0) (Pd₂(dba)₃, 0.1 g, 0.1 mmol), *rac*-BINAP (0.2 g, 0.3 mmol) and *t*-BuONa (1.7 g, 17.7 mmol) in toluene (200 mL) was purged with Ar, and benzophenone-imine (2.4 mL, 2.6 g, 14.6 mmol) was added. The reaction mixture was stirred at 110 °C for 24 h, evaporated to dryness in *vacuo* and the residue was separated by column chromatography (toluene/ethyl acetate 10:1, then chloroform/diethylether 50:1) to obtain triimine **5** (2.9 g, 3.59 mmol, 91 %). ¹H NMR (300 MHz, CDCl₃, 22° C): δ = 7.87-7.81 (m, 9H), 7.55-7.40 (m, 12H), 7.21 (s, 15H), 2.28

(s, 9H) ppm. ^{13}C APT NMR (75 MHz, CDCl_3 , 22° C): δ = 167.57 (C), 149.05 (C), 139.84 (C), 136.59 (C), 130.77 (CH), 129.51 (2xCH), 129.21 (2xCH), 128.90 (CH), 128.33 (2xCH), 128.18 (C), 128.13 (2x CH), 127.70 (C), 125.46 (C), 124.52 (CH), 113.18 (CH), 18.86 (CH_3) ppm. HRMS (ESI+): calcd. for $\text{C}_{60}\text{H}_{46}\text{N}_3$ $[M+H]^+$ 808.36862; found 808.36847.

3,7,11-trimethyltriphenylene-2,6,10-triamine (6): Triimine **5** (2.9 g, 3.59 mmol) was treated with 2 M aq. HCl (40 mL) in THF (100 mL) at room temperature for 2 h. The reaction mixture was neutralized by concentrated aq. NH_3 until basic and extracted with ethyl acetate. The combined organic phases were washed with water, dried over Na_2SO_4 , evaporated to dryness in *vacuo* and the crude product was separated by column chromatography (ethyl acetate) to obtain triamine **6** (1.0 g, 3.17 mmol, 88 %). ^1H NMR (300 MHz, $[\text{D}_6]$ DMSO, 22° C): δ = 7.92 (s, 3H), 7.60 (s, 3H), 5.03 (bs, 6H), 2.26 (s, 9H) ppm. ^{13}C APT NMR (75 MHz, $[\text{D}_6]$ DMSO, 22° C): δ = 145.86 (C), 129.51 (C), 124.09 (CH), 120.83 (C), 118.20 (C), 104.87 (CH), 17.95 (CH_3) ppm. HRMS (ESI+): calcd. for $\text{C}_{21}\text{H}_{22}\text{N}_3$ $[M+H]^+$ 316.18082; found 316.18099.

Tri-tert-butyl (3,7,11-trimethyltriphenylene-2,6,10-triyl)tri-carbamate (7): Triamine **6** (1.0 g, 3.17 mmol) was treated with Boc_2O (2.6 g, 11.9 mmol) in THF (100 mL) at reflux overnight. The reaction mixture was concentrated in a rotary evaporator and petroleum ether was added. The precipitated solid was filtered off, washed with petroleum ether and dried in *vacuo*. Boc-protected triamine **7** was obtained (1.8 g, 2.92 mmol, 92 %). ^1H NMR (300 MHz, $[\text{D}_6]$ DMSO, 22° C): δ = 8.77 (s, 3H), 8.60 (s, 3H), 8.34 (s, 3H), 2.46 (s, 9H), 1.53 (s, 27H) ppm. ^{13}C APT NMR (75 MHz, $[\text{D}_6]$ DMSO, 22° C): δ = 153.74 (C), 136.43 (C), 131.61 (C), 127.20 (C), 125.50 (C), 124.53 (CH), 118.25 (CH), 78.96 (C), 28.25 (CH_3), 18.25 (CH_3) ppm. HRMS (ESI+): calcd. for $\text{C}_{36}\text{H}_{45}\text{N}_3\text{O}_6\text{Na}$ $[M+\text{Na}]^+$ 638.32006; found 638.31970.

Tri-tert-butyl (3,7,11-tris(bromomethyl)triphenylene-2,6,10-triyl) tricarbamate (8): Triamine **7** (310 mg, 0.503 mmol) was treated with *N*-bromosuccinimide (NBS, 0.32 g, 1.80 mmol) and 2,2'-azobis(2-methylpropionitrile) (AIBN, 0.03 g, 0.18 mmol) in CCl_4 (60 mL) under irradiation by an IR lamp (250 W) for 8 h. The reaction mixture was evaporated to dryness in *vacuo* and water was added. The solid was filtered off, washed with water, methanol and petroleum ether, and dried in *vacuo* to obtain tribromide **8** (310 mg, 0.364 mmol, 73%). ^1H NMR (300 MHz, $[\text{D}_6]$ DMSO, 22° C): δ = 9.05 (s, 3H), 8.71 (s, 3H), 8.68 (s, 3H), 5.11 (s, 6H), 1.55 (s, 27H) ppm. ^{13}C APT NMR (75 MHz, $[\text{D}_6]$ DMSO, 22° C): δ = 153.69 (C), 136.91 (C), 130.79 (C), 129.80 (C), 126.25 (CH), 124.87 (C), 119.02 (CH), 79.50 (C), 31.93 (CH_2), 28.30 (CH_3) ppm. HRMS (ESI+): calcd. for $\text{C}_{36}\text{H}_{42}\text{Br}_3\text{N}_3\text{O}_6\text{Na}$ $[M+\text{Na}]^+$ 874.04934; found 874.04955.

Tri-tert-butyl (3,7,11-tris((naphthalen-2-ylamino)methyl)tri-phenylene-2,6,10-triyl)tricarbamate (9): Tribromide **8** (250 mg, 0.293 mmol) was reacted with 2-aminonaphthalene (0.25 g, 1.75 mmol) and K_2CO_3 (0.08 g, 0.58 mmol) in DMF (100 mL) at 50°C for 5 h. The reaction mixture was evaporated to dryness in *vacuo* and water was added. The solid was filtered off, washed with water, methanol, petroleum ether, and dried in *vacuo*. Hexamine **9** (262 mg, 0.252 mmol, 86%) was obtained by crystallization from tetrahydrofuran/hexane. ^1H NMR (500 MHz, $[\text{D}_6]$ DMSO, 22° C): δ = 8.92 (s, 1H, NH), 8.59 (s, 1H), 8.57 (s, 1H), 7.63 (br. d, $^3J(\text{H,H}) = 8.2$ Hz, 1H), 7.62 (d, $^3J(\text{H,H}) = 8.9$ Hz, 1H), 7.47 (br. d, $^3J(\text{H,H}) = 8.4$ Hz, 1H), 7.24 (ddd, $^3J(\text{H,H}) = 8.4$ Hz, $^4J(\text{H,H}) = 6.9$ Hz, $^5J(\text{H,H}) = 1.2$ Hz, 1H), 7.13 (dd, $^3J(\text{H,H}) = 8.9$ Hz, $^4J(\text{H,H}) = 2.1$ Hz, 1H), 7.09 (ddd, $^3J(\text{H,H}) = 8.2$ Hz, $^4J(\text{H,H}) = 6.9$ Hz, $^5J(\text{H,H}) = 1.1$ Hz, 1H), 6.75 (d, $^4J(\text{H,H}) = 2.1$ Hz, 1H), 6.67 (t, $^3J(\text{H,H}) = 5.9$ Hz, 1H, NH), 4.55 (2H, d, 5.5), 1.48 (9H, s) ppm. ^{13}C APT NMR (126 MHz, $[\text{D}_6]$ DMSO, 22° C): δ = 153.70 (C), 146.52 (C), 136.06 (C), 134.98 (C), 132.46 (C), 128.44 (CH), 128.17 (C), 127.42 (CH), 126.71 (C), 125.95 (CH), 125.47 (CH), 125.21 (C), 122.40 (CH), 121.21 (CH), 118.41 (2CH), 103.27 (CH), 79.28 (C), 43.45 (CH_2), 28.13 (CH_3) ppm. HRMS (ESI+): calcd. for $\text{C}_{66}\text{H}_{67}\text{N}_6\text{O}_6$ $[M+H]^+$ 1039.51166.; found 1039.51100.

Tris-TB 2: Hexaamine **9** (340 mg, 0.327 mmol) was dissolved in TFA (10 mL) and paraformaldehyde (140 mg, 2.91 mmol of CH₂O equiv.) was added. The reaction mixture was stirred at room temperature overnight. The reaction mixture was diluted with ice water, alkalized with concentrated aq. NH₃ and extracted with dichloromethane. The combined organic phases were washed with water, dried over Na₂SO₄, evaporated to dryness in *vacuo* and the residue was separated by column chromatography (dichloromethane/methanol 95:5) to obtain *calix-2* (48 mg, 59.1 μmol, 18%) and *throne-2*¹⁰ (154 mg, 0.190 mmol, 58%). *Calix-2*. ¹H NMR (500 MHz, CDCl₃, 22° C): δ = 8.14 (s, 3H), 8.02 (s, 3H), 7.70-7.46 (m, 9H), 7.40-7.17 (m, 9H), 5.08 (d, ³J(H,H) = 16.6 Hz, 3H), 4.96 (d, ³J(H,H) = 16.6 Hz, 3H), 4.65 (d, ³J(H,H) = 16.6 Hz, 3H), 4.60 (d, ³J(H,H) = 16.6 Hz, 3H), 4.57 (d, ³J(H,H) = 12.8 Hz, 3H), 4.51 (d, ³J(H,H) = 12.8 Hz, 3H) ppm. ¹³C APT NMR (126 MHz, CDCl₃, 22° C): δ = 147.50 (C), 144.67 (C), 131.15 (C), 130.80 (C), 129.21 (C), 128.55 (CH), 128.17 (CH), 127.09 (C), 126.52 (CH), 125.96 (C), 124.85 (CH), 124.36 (CH), 121.93 (CH), 121.31 (CH), 121.17 (C), 118.82 (CH), 67.08 (CH₂), 57.93 (CH₂), 57.85 (CH₂) ppm. HRMS (ESI+): calcd. for C₅₇H₄₃N₆ [*M*+H]⁺ 811.35437; found 811.35391.

5. References

- 1 SAINT. Bruker AXS Inc., Madison, Wisconsin, USA, 2015.
- 2 SADABS. Siemens Industrial Automation, Inc. SADABS: Area-Detector Absorption Correction; Madison, WI, 1996.
- 3 CrysAlisPro. Version 171.31.7 Oxford Diffraction Ltd, 68 Milton Park, Abingdon, Oxfordshire OX14 4RX, England, 2011.
- 4 APEX3. Bruker AXS Inc., Madison, Wisconsin, USA, 2003.
- 5 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, SIR92, *J. Appl. Cryst.*, 1994, **27**, 435.
- 6 P.W. Betteridge, J.R. Carruthers, R.I. Cooper, K. Prout and D.J. Watkin, CRYSTALS. *J. Appl. Cryst.*, 2003, **36**, 1487.
- 7 H. Bock, M. Rajaoarivelo, S. Clavaguera, É. Grelet, *Eur. J. Org. Chem.*, **2006**, *13*, 2889–2893.
- 8 Z. U. Levi, T. D. Tilley, *J. Am. Chem. Soc.* **2010**, *132*, 11012–11014.
- 9 a) A. Lebkücher, C. Wagner, O. Hübner, E. Kaifer, H.-J. Himmel, *Inorg. Chem.*, **2014**, *53*, 9876–9896; b) L. Chen, J. Kim, T. Ishizuka, Y. Honsho, A. Saeki, S. Seki, H. Ihee and D. Jiang, *J. Am. Chem. Soc.*, **2009**, *131*, 7287–7292.
- 10 *Throne-2*. ¹H NMR (500 MHz, CDCl₃, 22° C): δ = 8.14 (s, 2H), 8.12 (s, 1H), 8.00 (s, 1H), 7.75-7.73 (m, 9H), 7.47-7.21 (m, 9H), 5.17-4.32 (m, 18H) ppm. ¹³C APT NMR (126 MHz, CDCl₃, 22° C): δ = 147.83 (C), 144.98 (C), 131.25 (C), 131.19 (C), 130.84 (C), 130.80 (C), 130.79 (C), 129.22 (C), 128.67 (CH), 128.61 (CH), 128.59 (CH), 128.18 (CH), 128.16 (CH), 128.07 (CH), 127.05 (C), 126.99 (C), 126.60 (C), 126.57 (C), 126.53 (C), 125.89 (C), 125.83 (C), 124.90 (CH), 124.85 (CH), 124.52 (CH), 121.84 (CH), 121.82 (CH), 121.39 (CH), 121.34 (CH), 121.31 (CH), 118.81 (CH), 118.74 (CH), 67.01 (CH₂), 57.91 (CH₂), 57.83 (CH₂) ppm. HRMS (ESI+): calcd. for C₅₇H₄₃N₆ [M+H]⁺ 811.35437; found 811.35381.