Electronic Supporting Information

Self-assembled, optically-activate {naphthalene diimide}U{cucurbit[8]uril} ensembles in an aqueous environment

Heather F. Higginbotham,[a] Subashani Maniam,[b] Tina Hsia,[a] Lyle Isaacs,[c] Steven J. Langford[d] and Toby D. M. Bell.[a]

[a]School of Chemistry, Monash University, Clayton, Victoria 3800, Australia.

[b]Applied Chemistry and Environmental Science, School of Science, RMIT University, Melbourne, Victoria 3001, Australia.

[c]Department of Chemistry and Biochemistry, University of Maryland, College Park, MD, 20742, USA.

[d]Department of Chemistry and Biotechnology, Faculty of Science, Engineering & Technology, Swinburne University of Technology, Victoria 3122, Australia.

Contents

S1: Experimental methods

1,4,5,8-naphthalene tetracarboxylic dianhydride (Tokyo Chemical Industries), 4-amino-*N*-benzylpiperidine (Sigma Aldrich) pyridine-4-amine (Sigma Aldrich), *N*-benzyl ethylenediamine (Sigma Aldrich), *N*,*N*-diisopropylethylamine (Sigma Aldrich), and piperidine-4-amine (Sigma Aldrich) were used without further purification. Solvents, acetic acid and dichloromethane (Merck) were used as received, and aqueous solutions prepared using MilliQ water.

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded using a Bruker DRX 400 MHz Spectrometer (^{1}H taken at 400 MHz) or Bruker DRX 600 MHz Spectrometer (^{13}C taken at 125 MHz), using deuterated chloroform and DMSO. The chemical shifts (δ) were calibrated with reference to the solvent peak in the spectrum. For ^{1}H NMR spectra, each resonance was assigned according to the following convention: chemical shift (d), measured in parts per million (ppm), multiplicity, coupling constant (J), measured in Hz, number of protons and assignment. Multiplicities are given as (s) singlet, (d) doublet, (t) triplet, (q) quartet, (p) pentet or (m) multiplet. The ^{13}C NMR spectra were assigned a chemical shift (δ) measured in parts per million. Low resolution electrospray ionisation mass spectrometry (LR-MS) was performed on a Micromass Platform API QMS-quadrupole electrospray mass spectrometer. Spectra were taken in either positive ion mode (ESI^+) or negative ion mode (ESI^-), with $[M]^+$ or $[M]^-$ denoting the molecular ion for each mode respectively. High resolution electrospray ionisation mass spectrometry (HR-MS) was performed on an Agilent Technologies 6220 Accurate-Mass TOF instrument. Spectra were taken in positive ion mode (ESI^+), with $[M]^+$ denoting the molecular ion for each mode respectively. Melting point was performed using a Stuart scientific melting point apparatus with melting points denoted in degrees Celsius (°C).

Steady state spectroscopic characterisation: Absorbance spectra were run on a Cary100 Bio UV-visible spectrophotometer (Agilent technologies) and steady state fluorescence measurements were recorded on a Varian model Cary Eclipse fluorescence spectrophotometer (Agilent technologies) and corrected for detector efficiency. Solutions were prepared in clean 1.0 cm quartz cuvettes. For quantum yield measurements absorbance maxima were less than 0.10 in order to reduce inner filter effects and samples were deoxygenated by bubbling with nitrogen for 20 min immediately prior to measurement. Emission spectra were taken under identical conditions and the areas under the curves integrated and compared to that of a solution of quinine sulfate in 0.5 M H_2SO_4 in water as the quantum yield reference standard ($QY_{flu} = 0.55$)[1] in order to determine fluorescence quantum yields. Differences in the fractions of light absorbed by the sample and reference solutions were accounted for using appropriate corrections.

Time Correlated Single Photon Counting: Fluorescence decay histograms were obtained using Time Correlated Single Photon Counting (TCSPC). The excitation source was a 375 nm pulsed diode (Picoquant LDH-P-C-375) providing pulses of >70 ps FWHM. Emission from the sample was collected at 90° to excitation light, passed through a monochromator (CVI, dk480) and focused onto a fast response avalanche photodiode detector (APD, Id-Quantique, Id-100). Photon emission times were recorded by a photon counting card (Picoquant, PicoHarp 300), with START signal provided by a sync out from the excitation laser and STOP signal provided by the APD detector. An instrument response function (IRF) recorded from a scattering solution (dilute milk powder in water) had a full width half maximum of ~96-130 ps.[2] Timed intervals between the START and STOP signals were histogrammed in 4-32 ps bins to produce a decay profile representing time versus photon counts. Fluorescence decay times were obtained by fitting the histogram with an exponential decay function (using either single, double or multi-exponential decay functions) convolved with an IRF using an iterative least-squares routine based on the Levenberg-Marquardt algorithm (TRFA Global Analysis program version 1.0 Scientific Software Technologies). Goodness of fit was determined using both the quality of the chi-squared parameter (χ^2) and by inspection of the residuals (data minus fit) which should be randomly distributed around zero for well-fit data.

S2: Synthetic procedures and NMR spectra

2,7-bis(1-benzylpiperidin-4-yl)benzo[*l*,*m*,*n*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone (NDI1)

4-Amino-*N*-benzylpiperidine (0.28 g, 1.5 mmol) was added to a suspension of 1,4,5,8 tetracarboxylic naphthalene dianhydride (0.20 g, 0.74 mmol) in 60 mL of glacial acetic acid and heated to 120 °C for 4 hours. The reaction mixture was then cooled to room temperature and washed with a saturated solution of $NaHCO_3$ and extracted into DCM. The crude product was then recrystallised from ethyl acetate/ *n*-hexanes/DMSO, yielding 0.38 g (83%) of (**NDI1**) as yellow crystals.

^{1}H NMR (400 MHz, $CHCl_3$) δ 8.72 (s, 4H, ArH), 7.41-7.28 (m, 10H, ArH), 5.08-4.99 (m, 2H, CH), 3.60 (s, 4H, C*H*$_2$-benzyl), 3.07-3.04 (m, 4H, CH_2), 2.94-2.83 (m, 4H, CH_2), 2.23-2.17 (m, 4H, CH_2), 1.73-1.68 (m, 4H, CH_2).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.4, 138.8, 131.1, 129.2, 128.4, 127.1, 127.0, 126.7, 62.8, 53.6, 53.0, 28.3.

Mass spectrum LR-MS (ESI, +ve): *m/z* 613.3 $[M+H]^+$

Mass spectrum HR-MS (ESI, +ve): *m/z* observed $[M+H]^+$ 613.2817, calculated $C_{38}H_{37}N_4O_4$ $[M+H]^+$ 613.2815.

2,7-di(pyridine-4-yl) benzo[*l*,*m*,*n*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone (NDI2)

Pyridin-4-amine (0.57 g, 6.0 mmol) was added to a suspension of 1,4,5,8 tetracarboxylic naphthalene dianhydride (0.80 g, 3.0 mmol) in 60 mL of glacial acetic acid and heated to 120 °C for 4 hours. The reaction mixture was then cooled to room temperature and the resulting precipitate was filtered under vacuum and dried, yielding 1.0 g (80%) of (**NDI2**) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.22 (apparent-d, 4H, ArH), 8.80 (s, 4H, ArH), 8.31 (apparent-d, 4H, ArH).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 162.5, 151.9, 143.7, 131.2, 128.8, 127.2, 127.1.

Mass spectrum HR-MS (ESI, -ve): *m/z* observed $[M]^-$ 420.0858, calculated $C_{24}H_{12}N_4O_4$ $[M]^-$ 420.0859.

2,7-bis(2(benzylamino)ethyl)benzo[*l*,*m*,*n*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone (NDI3)

N-benzyl ethylenediamine (0.22 g, 1.5 mmol) was added to a suspension of 1,4,5,8 tetracarboxylic naphthalene dianhydride (0.20 g, 0.74 mmol) in 60 mL of glacial acetic acid and heated to 120 °C for 4 hours. The reaction mixture was then cooled to room temperature and washed with a saturated solution of $NaHCO_3$ and extracted into DCM. The crude product was then recrystallised from DCM/ethyl acetate/ *n*-hexanes, yielding 0.35 g (87%) of (**NDI3**) as yellow crystals.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 4H, ArH), 7.28-7.16 (m, 10H, ArH), 4.40-4.36 (m, 4H, CH), 3.84 (apparent-s, 4H, ArH), 3.05-3.02 (m, 4H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 140.3, 131.1, 128.5, 128.2, 127.1, 126.9, 126.8, 53.6, 46.9, 40.5.

Mass spectrum LR-MS (ESI, +ve): *m/z* 533.3 $[M +H]^+$

Mass spectrum HR-MS (ESI, +ve): *m/z* observed $[M+H]^+$ 533.2189, calculated $C_{32}H_{29}N_4O_4$ $[M+H]^+$ 533.6080.

1-butylpiperidin-4-amine

N,*N*-diisopropylethylamine (1.70 mL, 9.98 mmol) was added to a mixture of piperidine-4-amine (1.0 g, 9.98 mmol) and 1-bromobutane (1.30 mL, 12.0 mmol) in 40 mL of chloroform and heated at reflux for 3 hours. Then the solvent was evaporated and the resulting crude product was diluted with 40 mL of dichloromethane, washed with water (3×30 mL) and reduced under vacuum, yielding 0.90 g (58%) of the title compound as a light yellow oil.

^{1}HNMR (400 MHz, $CHCl_3$) δ 2.81-2.77 (m, 2H, CH_2), 2.61-2.53 (m, 1H, CH), 2.25-2.21 (m, 2H, CH_2), 1.93-1.86 (m, 2H, CH_2), 1.78-1.73 (m, 2H, CH_2), 1.42-1.01 (m, 8H, CH_2 & NH_2), 0.86 (t, *J* = 7.2, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ 58.6, 52.7, 48.9, 36.2, 29.4, 20.9, 14.8

Mass spectrum LR-MS (ESI, +ve): *m/z* 157.2 $[M+H]^+$

2,7-bis(1-butylpiperidin-4-yl)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (NDI4)

1-butylpiperidin-4-amine (0.18 g, 1.1 mmol) was added to a suspension of 1,4,5,8 tetracarboxylic naphthalene dianhydride (0.10 g, 0.37 mmol) in 40 mL of dimethylformamide and heated at 80 °C for 12 hours. The resulting precipitate was filtered while the reaction solution was still hot. The solid was washed with 20 mL of methanol and 20 mL of *n*-hexane, yielding 130 mg (74%) of the title compound as a beige powder.

^{1}HNMR (400 MHz, $CHCl_3$) δ 8.71 (s, 4H, ArH), 5.04-4.98 (m, 2H, CH), 3.11-3.08 (m, 4H, CH_2), 2.92-2.82 (m, 4H, CH_2), 2.41-2.38 (m, 4H, CH_2), 2.16-2.10 (m, 4H, CH_2), 1.70-1.67 (m, 4H, CH_2), 1.55-1.48 (m, 4H, CH_2), 1.40-1.31(m, 4H, CH_2), 0.94 (t, *J* = 7.2, 6H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 131.1, 127.0, 126.7, 58.3, 53.9, 53.2, 29.6, 28.4, 21.0, 14.3.

Mass spectrum LR-MS (ESI, +ve): *m/z* 545.2 $[M+H]^+$

Mass spectrum HR-MS (ESI, +ve): *m/z* observed $[M+H]^+$ 545.3120, calculated $C_{32}H_{41}N_4O_4$ $[M+H]^+$ 545.3122.

2-(2-ethylhexyl)-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinoline-6,7-dicarboxylic acid

Synthesis was undertaken according to literature.[3] 1,4,5,8-Naphthalene tetracarboxylic dianhydride (2.80 g, 10.4 mmol) was suspended in water (400 mL). KOH pallets were added while stirring until complete dissolution of the starting material. The pH of the solution was adjusted to 6.4 with 1 M phosphoric acid solution addition. (2-ethyl)hexylamine (1.34 g, 10.4 mmol) was added and the pH was adjusted to 6.4 using 1 M phosphoric acid solution. The reaction mixture was heated at reflux for 12 hours. The reaction was allowed to cool to room temperature and acidified to pH 1-2 with glacial acetic acid. The precipitation formed was filtered and washed with methanol (50 mL) and *n*-hexane (50 mL) to give **2** as a white solid (2.50 g, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 7.6, 2H, NDI), 8.18 (d, *J* = 7.6, 2H, NDI), 4.05-3.93 (m, 2H, NCH_2), 1.87-1.84 (m, 1H, CH), 1.35-1.24 (m, 8H, CH_2), 0.89-0.83 (m, 6H, CH_3).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.5, 163.2, 136.9, 130.2, 129.2, 128.6, 125.5, 124.5, 43.5, 37.2, 30.2, 28.1, 23.6, 22.4, 13.9, 10.5.

HRMS (ESI) *m/z* obsd $[M+H]^+$ 398.1598, calcd $C_{22}H_{24}NO_6$ $[M+H]^+$ 398.1598.

2-(1-benzylpiperidin-4-yl)-7-(2-ethylhexyl)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (NDI5)

A mixture of 2-(2-ethylhexyl)-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinoline-6,7-dicarboxylic acid (200 mg, 0.50 mmol) and 1-benzylpiperidin-4-amine (105 mg, 0.55 mmol) in acetic acid (30 mL) was heated at reflux for 8 h. Then, the reaction was cooled to room temperature which resulted in the formation of crystalline solid precipitates. The solid was collected by filtration. The crude product was purified by recrystallization from DCM/methanol to obtain the final products as a yellow solid (248 mg, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 4H, NDI), 7.40-7.28 (m, 5H, Ar-H), 5.07-4.99 (m, 1H, CH), 4.18-4.08 (m, 2H, CH_2), 3.62 (apparent s, 2H, CH_2), 3.08-3.05 (m, 2H, CH_2), 2.95-2.85 (m, 2H, CH_2), 2.25-2.19 (m, 2H, CH_2), 1.92-1.86 (m, 1H, CH), 1.68-1.65 (m, 2H, CH_2), 1.40-1.29 (m, 8H, CH_2), 0.95-0.91 (m, 3H, CH_3), 0.89-0.85 (m, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 163.3, 131.12, 131.06, 129.2, 128.6, 128.4, 127.2, 127.1, 126.8, 126.7, 126.5, 62.6, 53.5, 52.9, 52.2, 44.7, 38.1, 30.8, 28.8, 28.2, 24.2, 23.6, 23.2, 14.2, 10.7.

HRMS (ESI) *m/z* observed $[M+H]^+$ 552.2857, calculated $C_{34}H_{38}N_3O_4$ $[M+H]^+$ 552.2857.

Synthetic procedures: NMR Spectral Data for Compounds NDI1-5

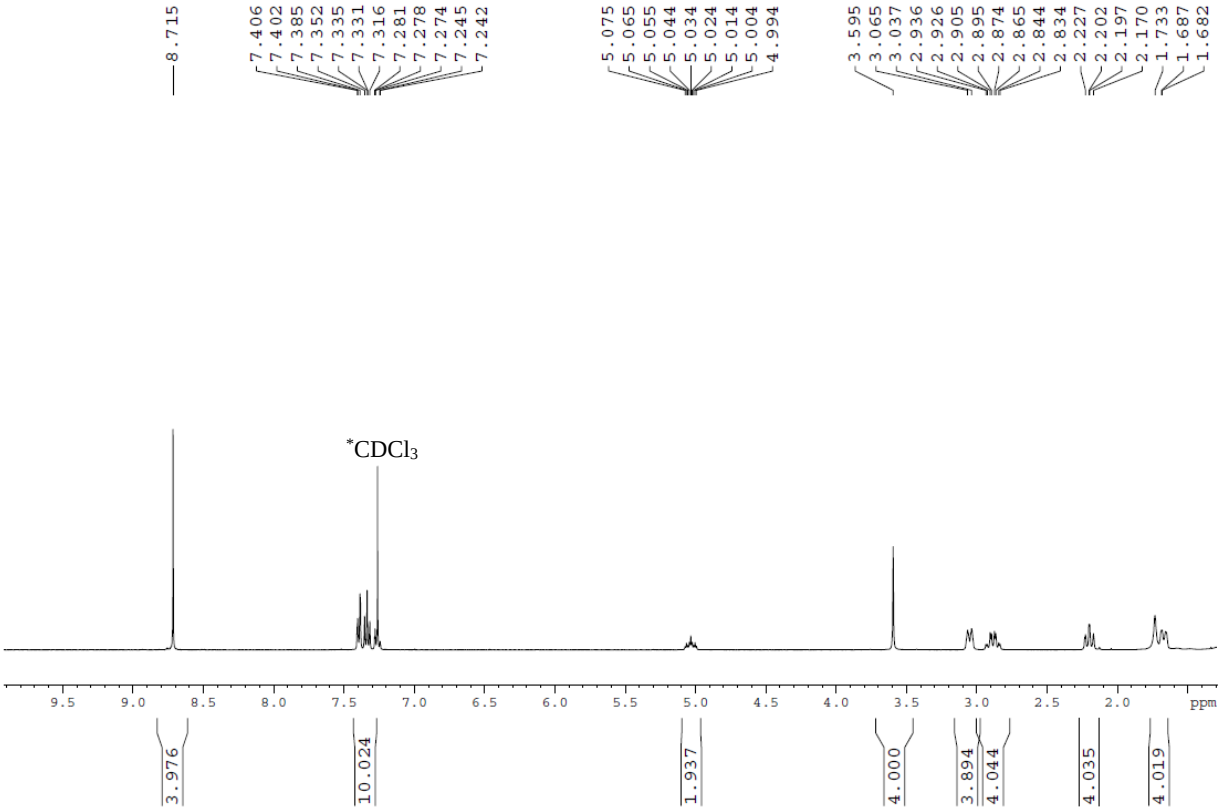


Figure S2.1: ^{1}H NMR (400 MHz, 300 K) spectrum of **NDI1** in $CDCl_3$.
*residual protons of deuterated solvent.

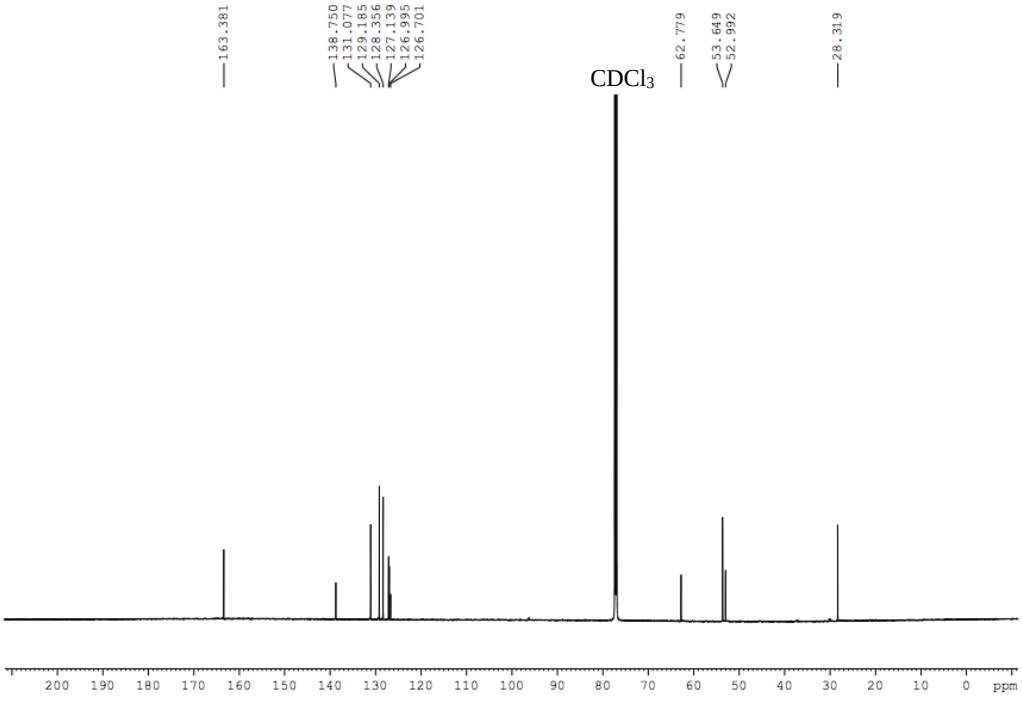


Figure S2.2: ^{13}C NMR (125 MHz, 300 K) spectrum of **NDI1** in $CDCl_3$.

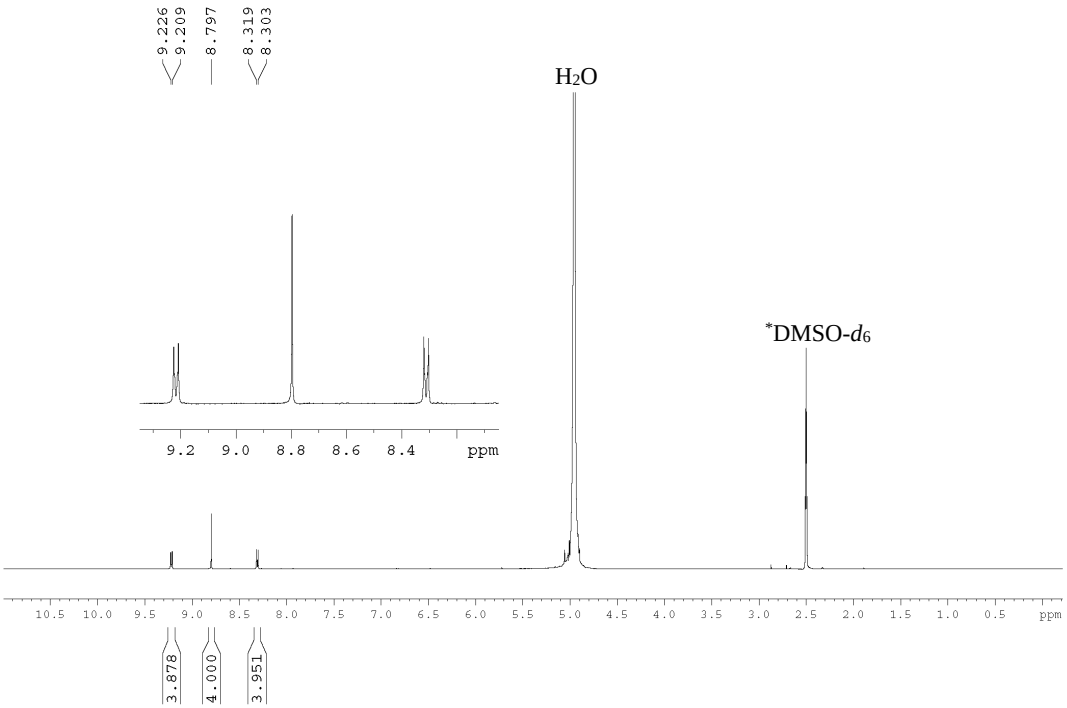


Figure S2.3: ^{1}H NMR (400 MHz, 300 K) spectrum of **NDI2** in DMSO-d_6.
*residual protons of deuterated solvent.

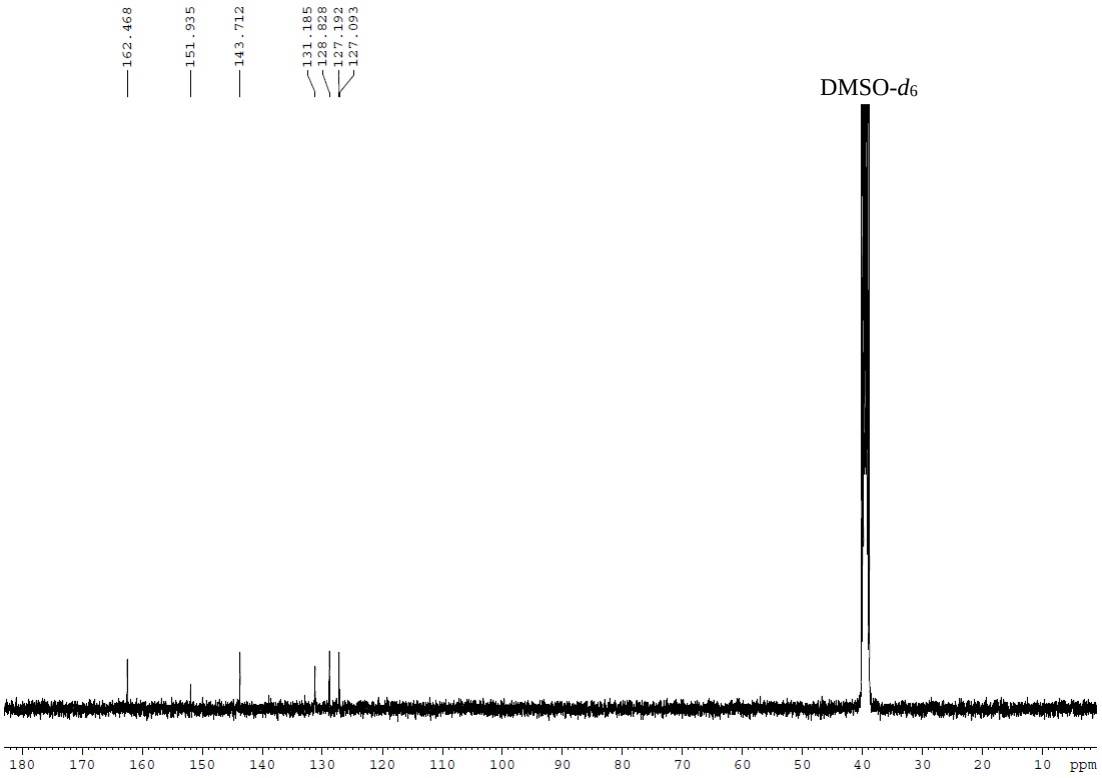


Figure S2.4: ^{13}C NMR (100 MHz, 300 K) spectrum of **NDI2** in DMSO-d_6.

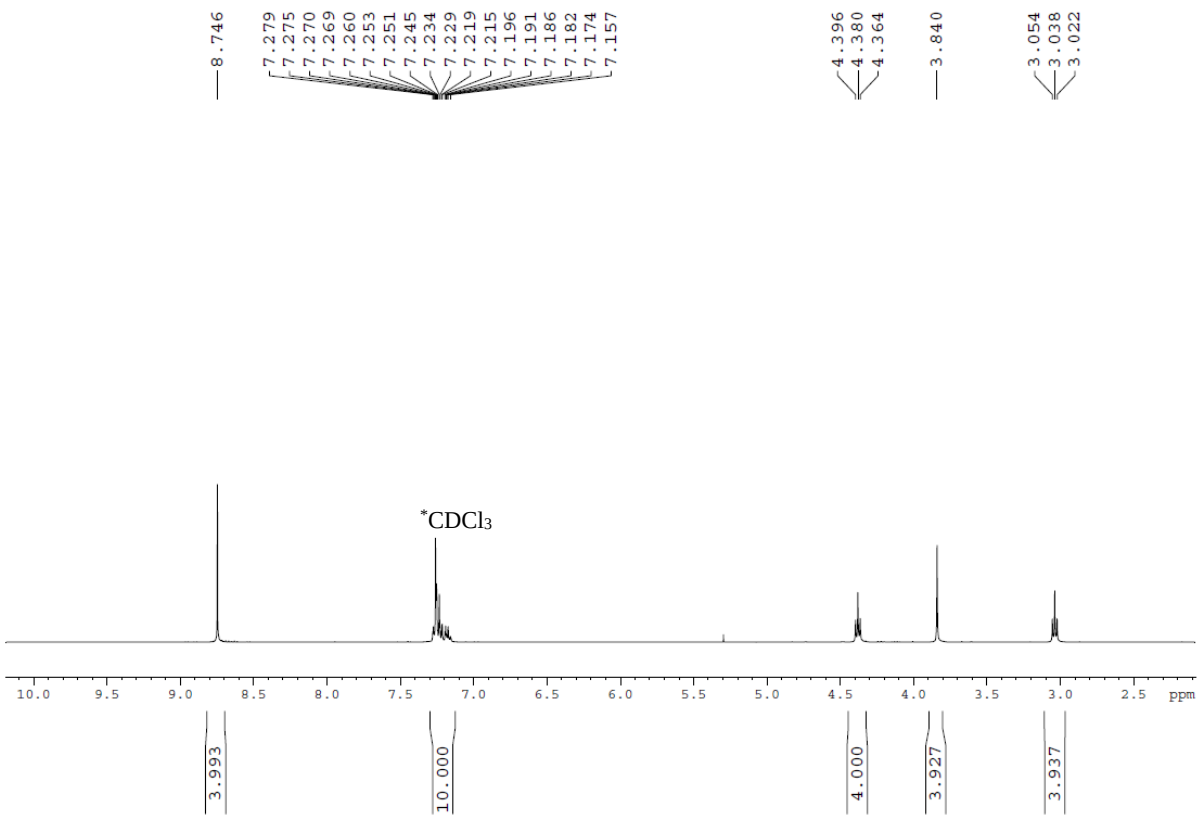


Figure S2.5: ^{1}H NMR (400 MHz, 300 K) spectrum of **NDI3** in $CDCl_3$.
*residual protons of deuterated solvent.

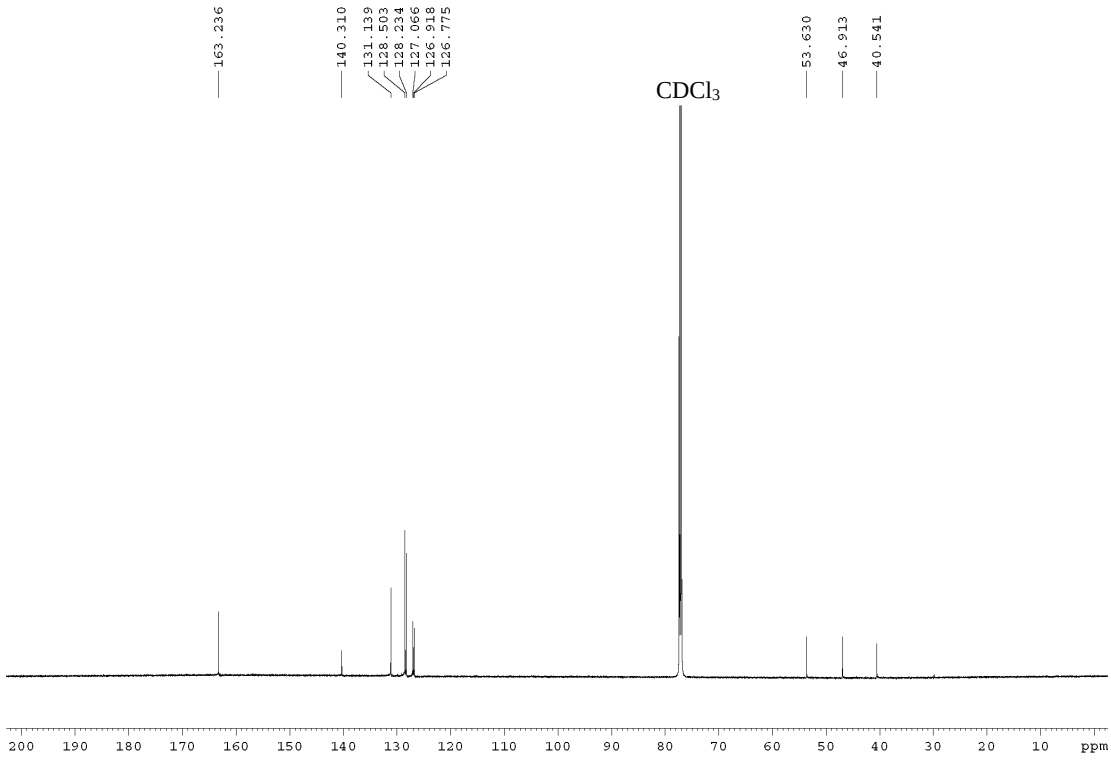


Figure S2.6: ^{13}C NMR (100 MHz, 300 K) spectrum of **NDI3** in $CDCl_3$.

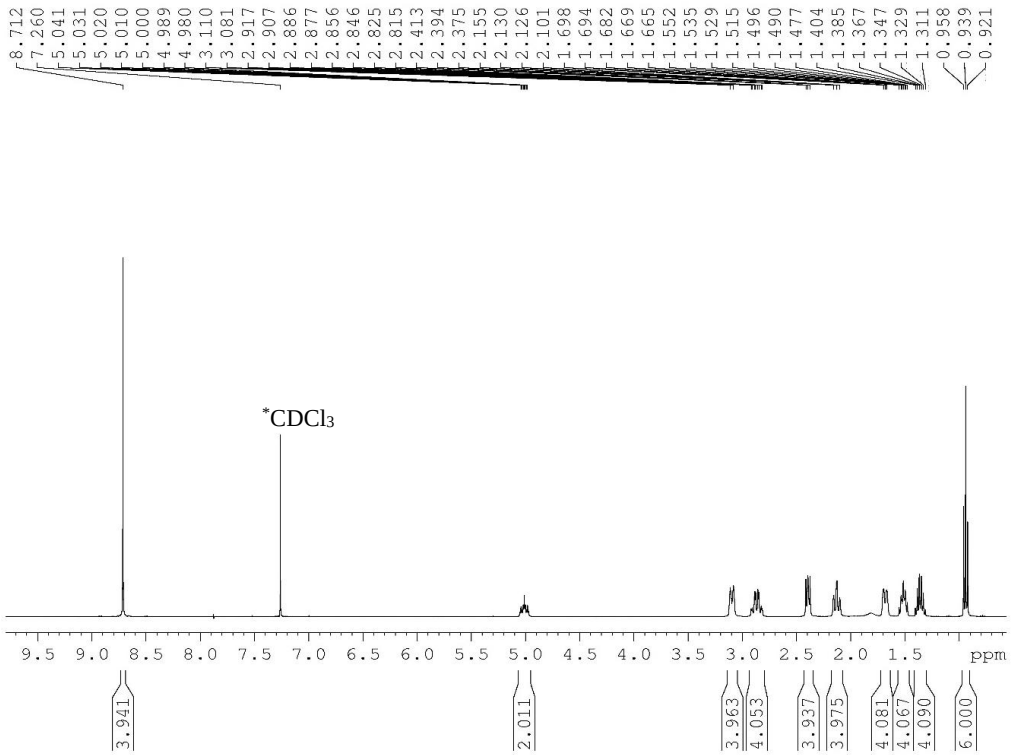


Figure S2.7: ^{1}H NMR (400 MHz, 300 K) spectrum of **NDI4** in $CDCl_3$.
*residual protons of deuterated solvent.

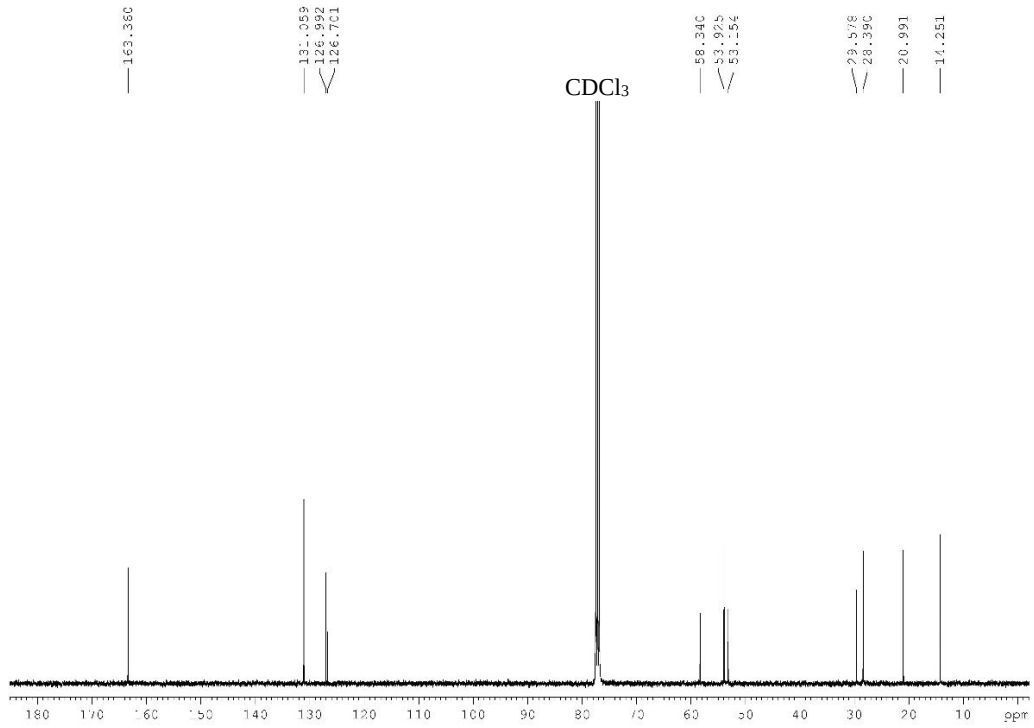


Figure S2.8: ^{13}C NMR (100 MHz, 300 K) spectrum of **NDI4** in $CDCl_3$.

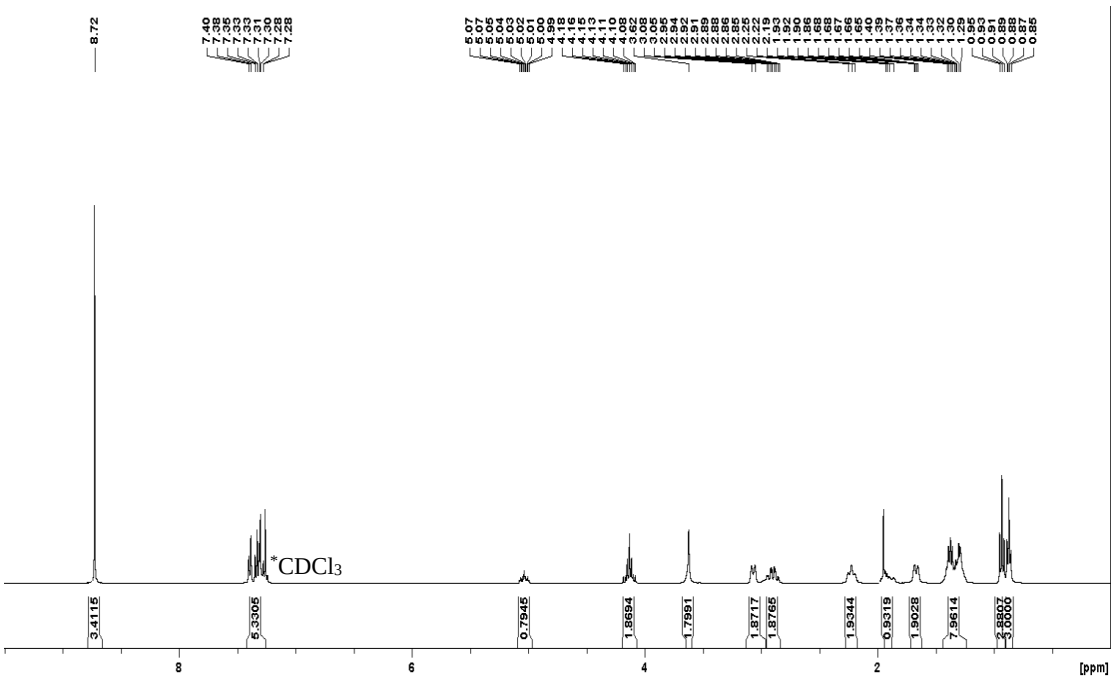


Figure S2.9: ^{1}H NMR (400 MHz, 300 K) spectrum of **NDI5** in $CDCl_3$.
*residual protons of deuterated solvent.

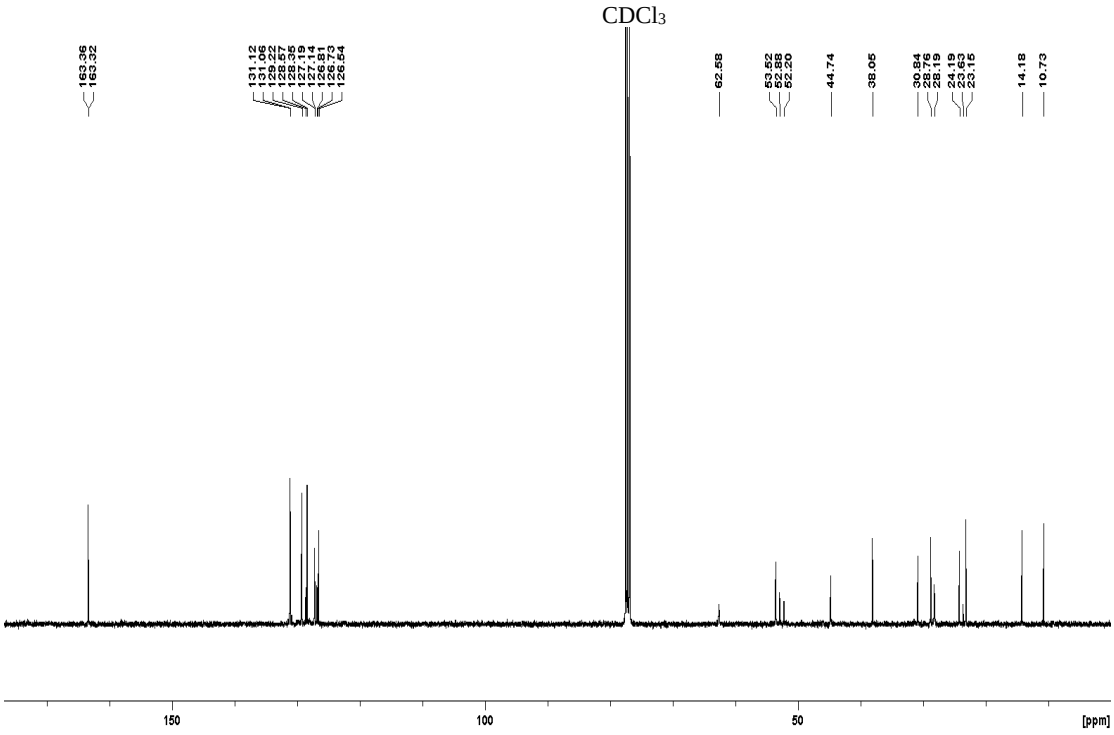


Figure S2.10: ^{13}C NMR (100 MHz, 300 K) spectrum of **NDI5** in $CDCl_3$.

S3: Crystallographic data of NDI1.CB[8]

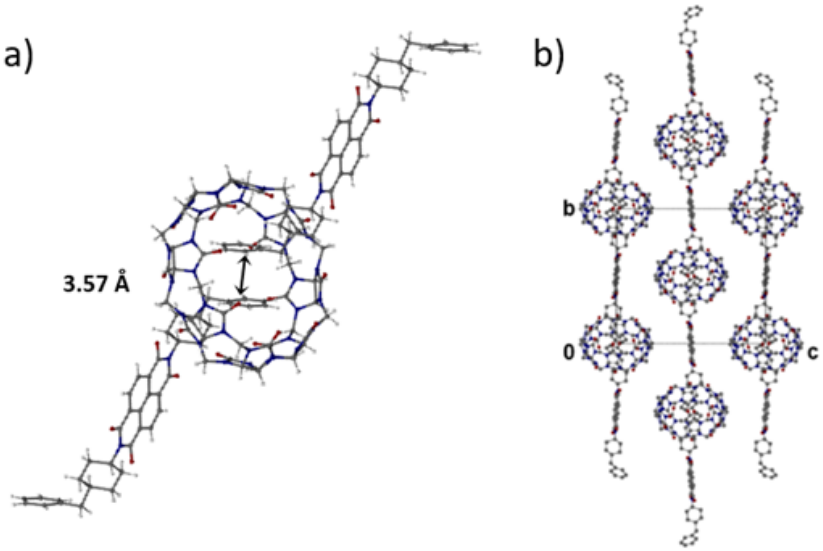


Figure S3.1: a) **NDI1**•CB[8] complex showing insertion of benzyl groups from two separate **NDI1** molecules into the same CB[8] cavity, and b) the packing diagram as viewed down the crystallographic *a* axis.

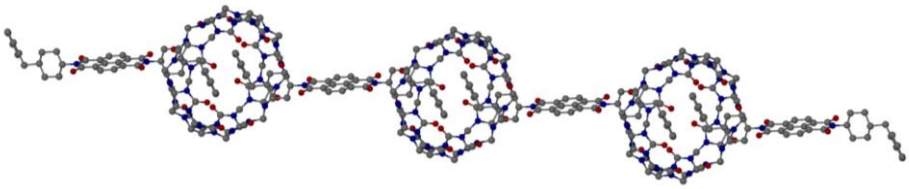


Figure S3.2: Part of a continuous supramolecular chain of molecules lying along the *b* axis.

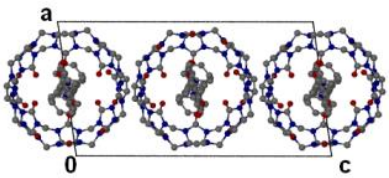


Figure S3.3: Packing diagrams as viewed down the *b* axis.

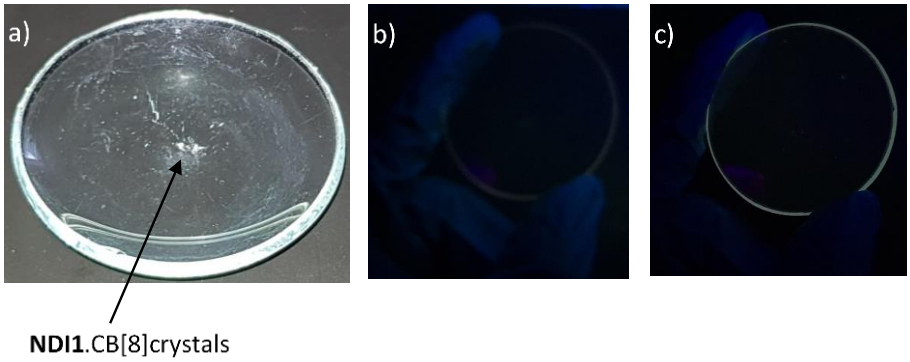
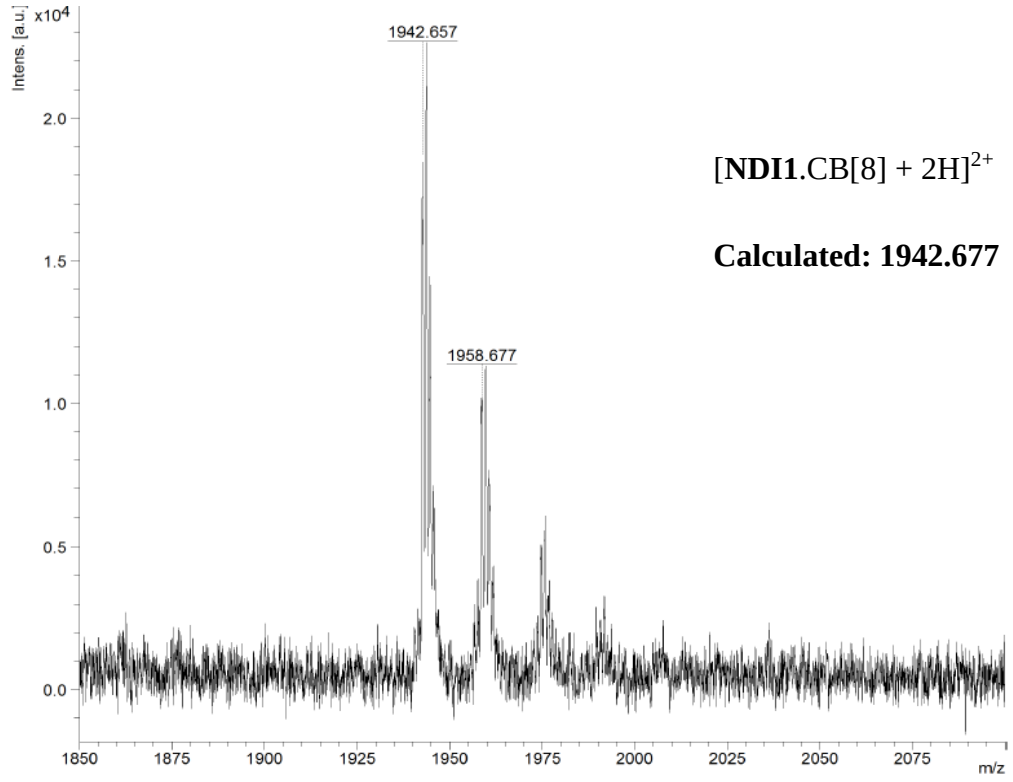


Figure S3.4: Images of **NDI1**•CB[8] crystals under a) visible light, b), c) UV light 365 nm and 254 nm, respectively. Only extremely weak violet emission consistent with NDI monomers is observed under UV excitation.

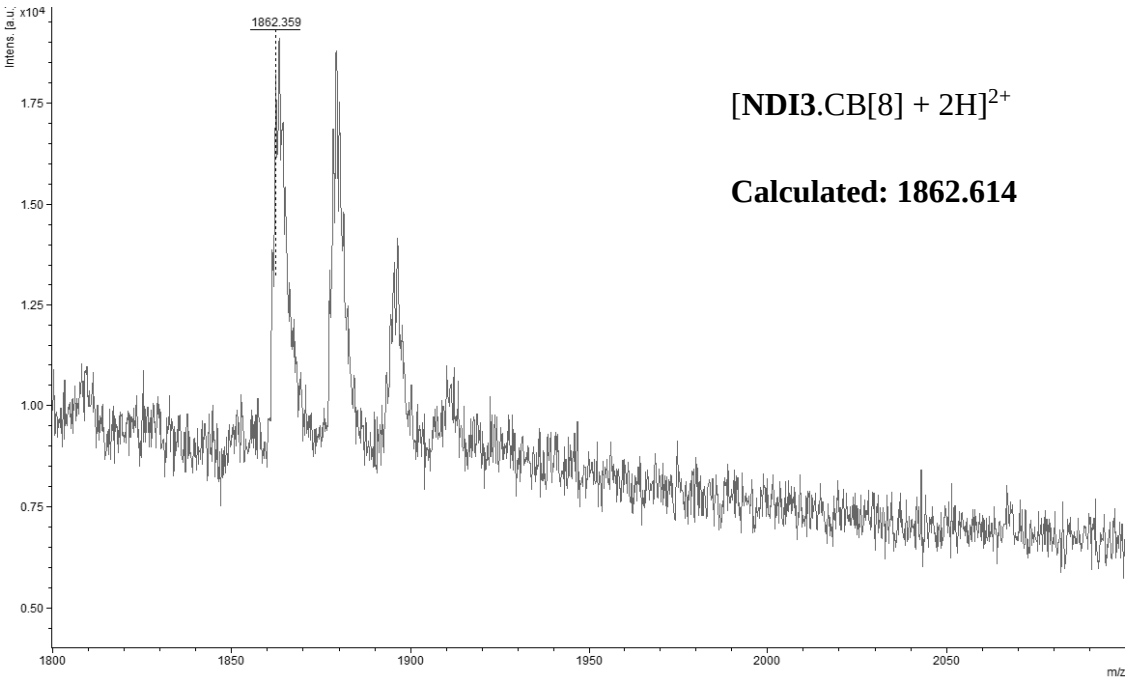
S4: Mass spectroscopic data



[**NDI1**.CB[8] + 2H]$^{2+}$

Calculated: 1942.677

Figure S4.1: Mass spectrum of 2:2 **NDI1**.CB[8].



[**NDI3**.CB[8] + 2H]$^{2+}$

Calculated: 1862.614

Figure S4.2: Mass spectrum of 2:2 **NDI3**.CB[8].

S5: Determination of binding constant of NDI1•CB[8]

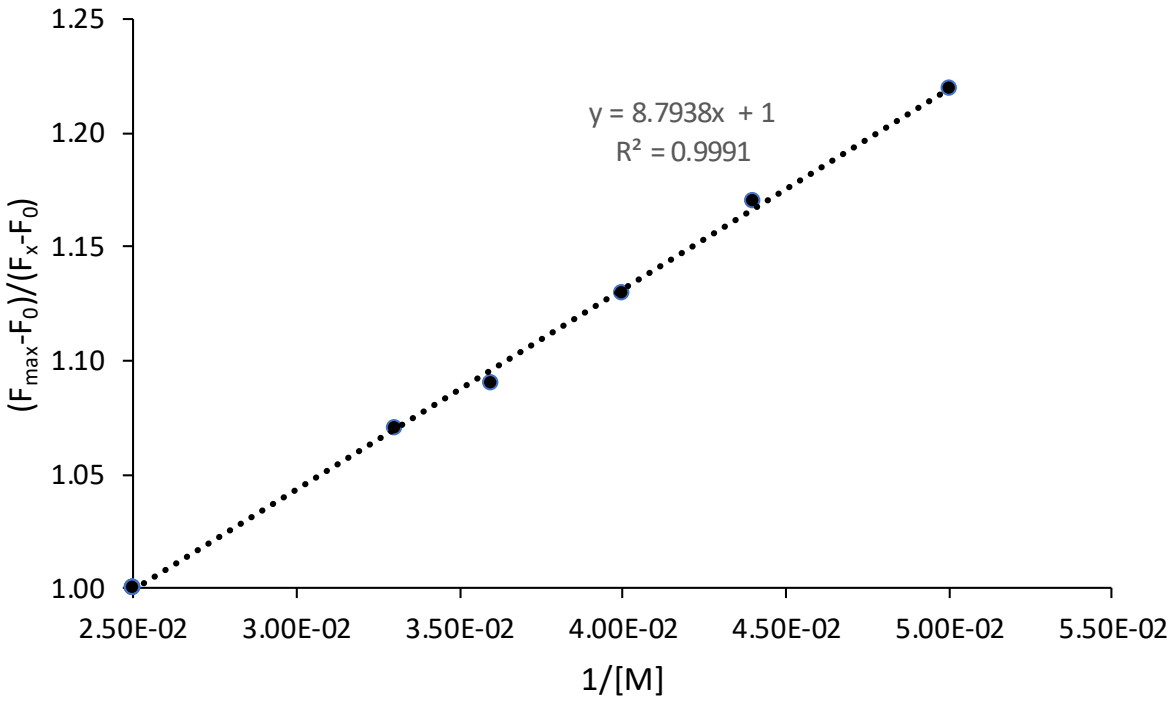


Figure S5.1: Binding constant curve and fitted function of **NDI1**•CB[8] derived from fluorescence titration data. The 2:2 binding constant of **NDI1** and CB is estimated from a modified Benesi-Hildebrand equation, $(F_{max} - F_0) / (F_x - F_0) = 1 + (1/K) (1/[M]^n)$ as reported by Sahana et al.[4] From the plot of $(F_{max} - F_0) / (F_x - F_0)$ against $1/[M]^n$, the value of K is determined from the slope. The assumption made is that the fluorescence change is only induced by the formation of a 2:2 complex between **NDI1** and CB.

S6: Additional steady-state spectral data

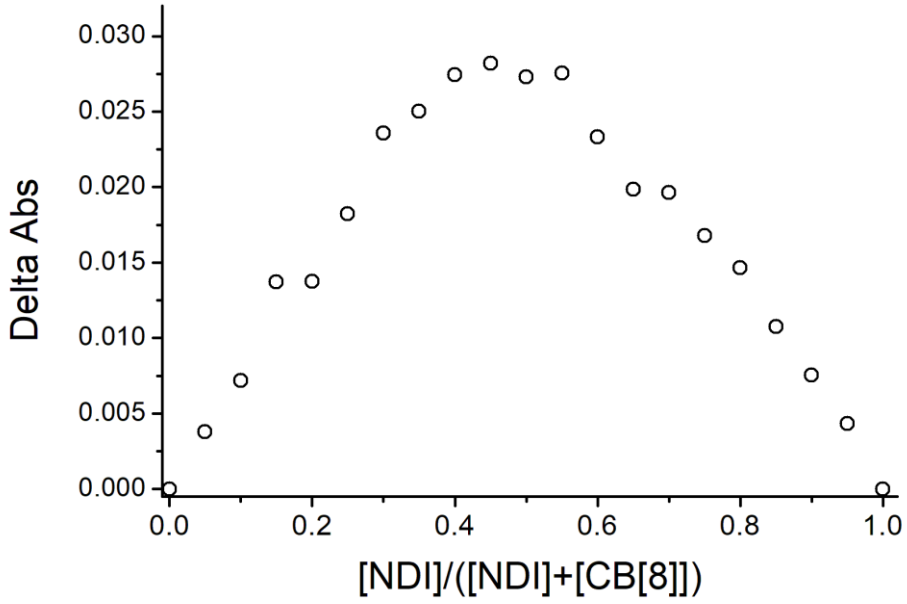


Figure S6.1: a) Job's plot of **NDI1** with CB[8] determined with the total concentration of ([NDI]+[CB[8]]) kept constant at 10 µmolL^{-1} in 0.1% TFA in water. Plot shown is the average of two separate measurements taken under the same conditions.

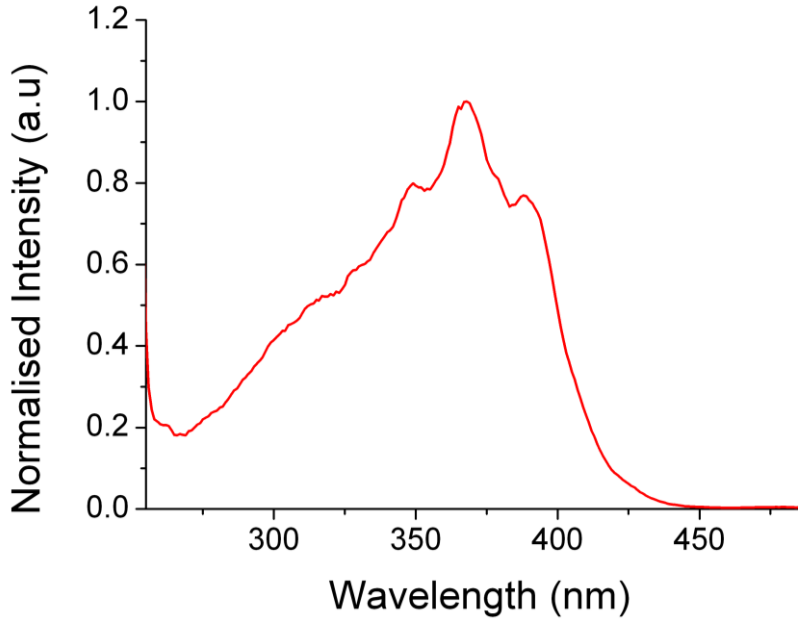


Figure S6.2: Normalised excitation spectrum (λ_{em} = 500 nm) of **NDI1** with 2 equivalents of CB[8] in 0.1% TFA in water.

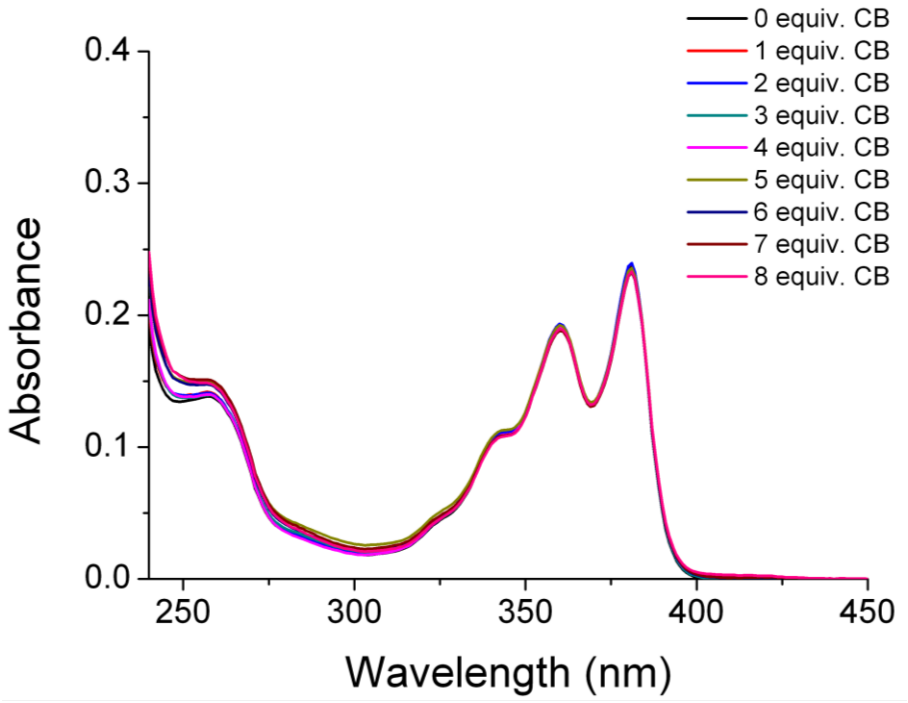


Figure S6.3: Absorption spectra of **NDI2** in 0.1% TFA in water with 0-8 equivalents of CB[8].

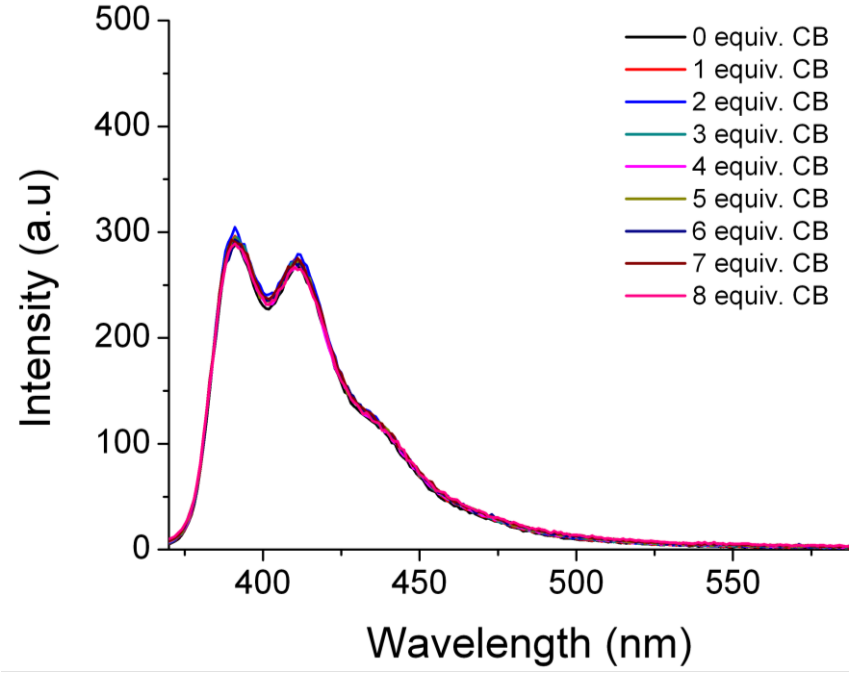


Figure S6.4: Emission spectra (λ_{ex}= 350 nm) of **NDI2** in 0.1% TFA in water with 0-8 equivalents of CB[8].

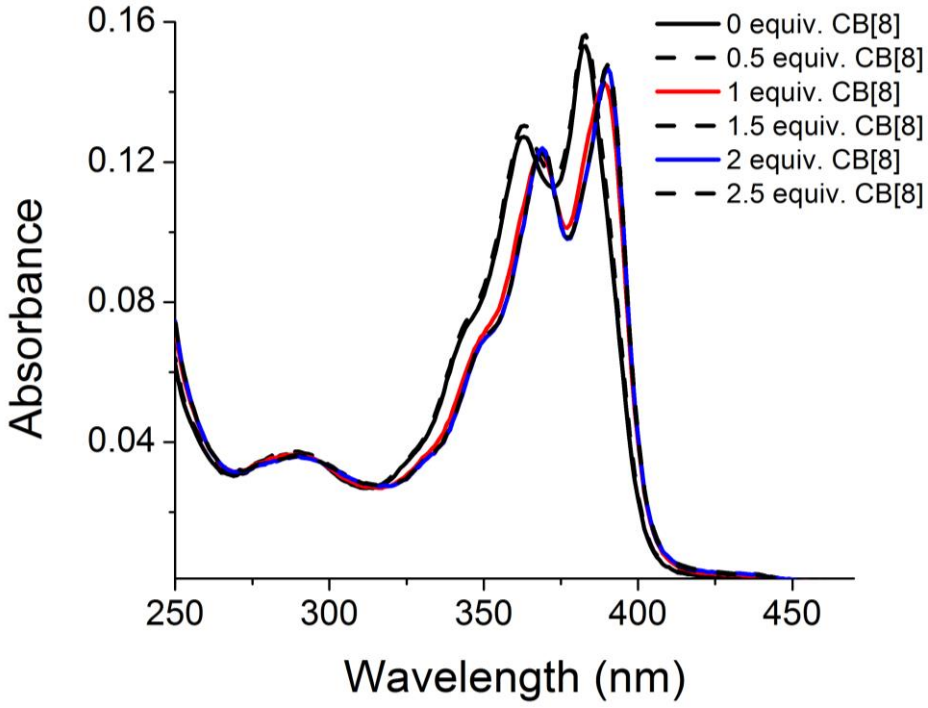


Figure S6.5: Absorption spectra of **NDI3** in 0.1% TFA in water with half-equimolar titrations of CB[8].

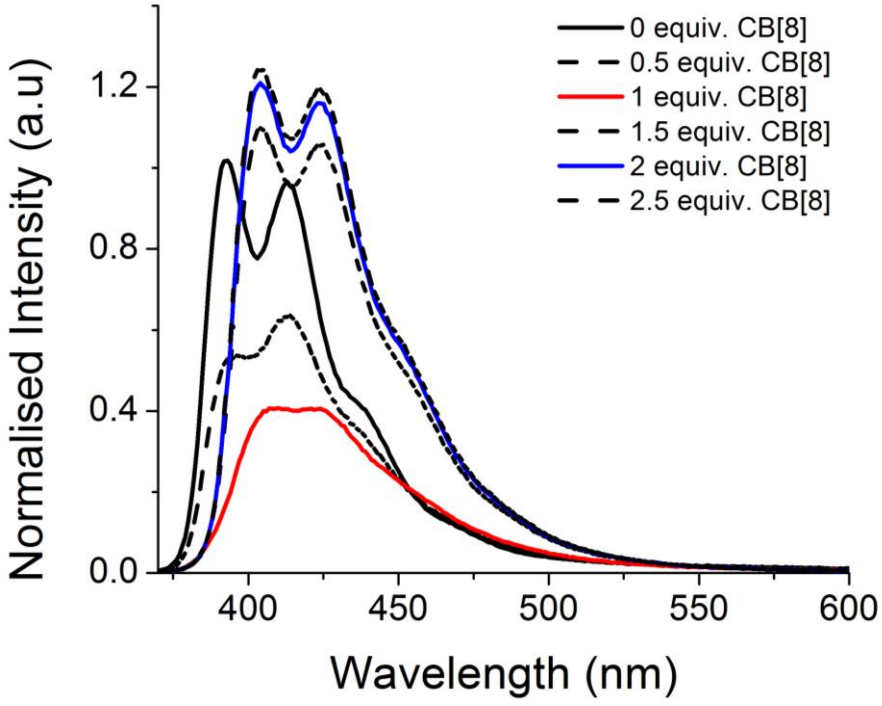


Figure S6.6: Emission spectra of **NDI3** in 0.1% TFA in water with half-equimolar titrations of CB[8].

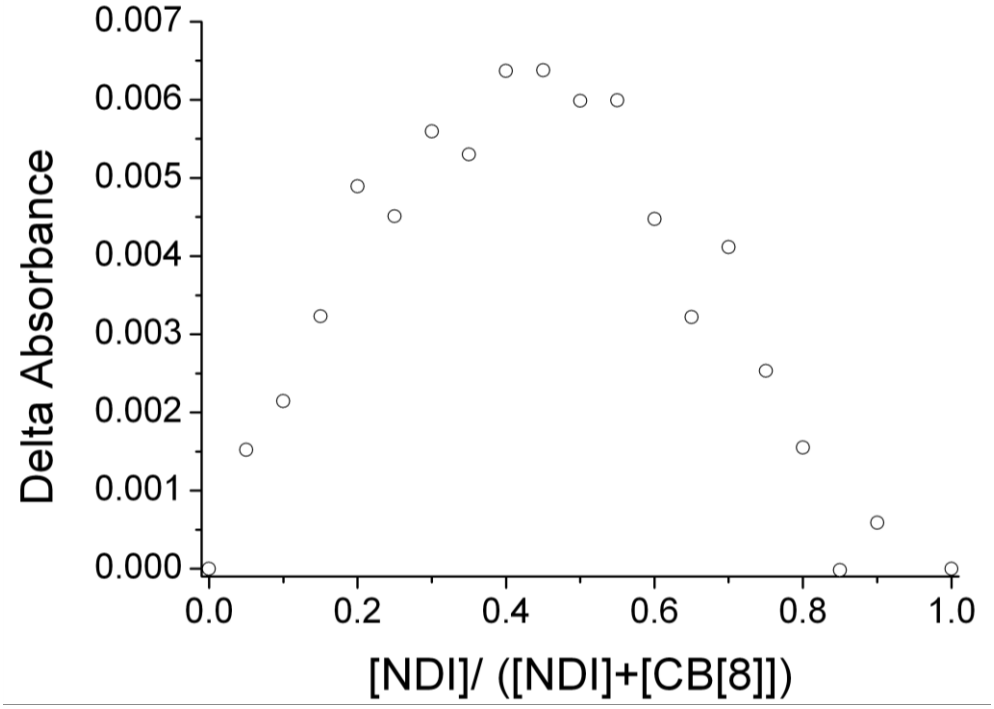


Figure S6.7: Job's plot of **NDI3** with CB[8**]** determined with the total concentration of ([NDI]+[CB[8]]) kept constant at 10 µmol L^{-1} in 0.1% TFA in water.

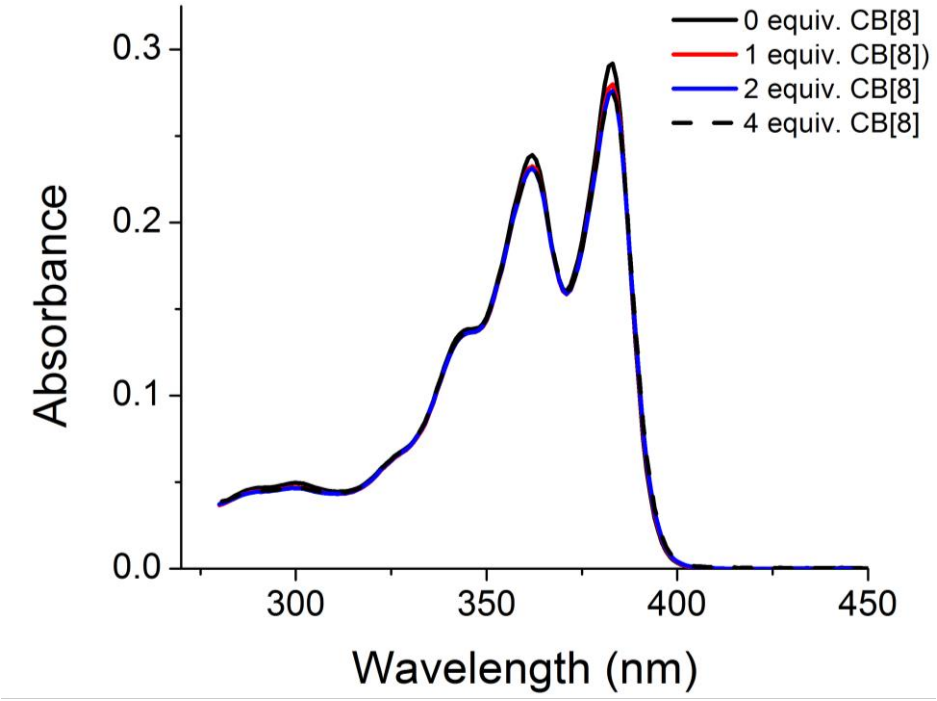


Figure S6.8: Absorption spectra of **NDI4** in 0.1% TFA in water with equimolar titrations of CB[8].

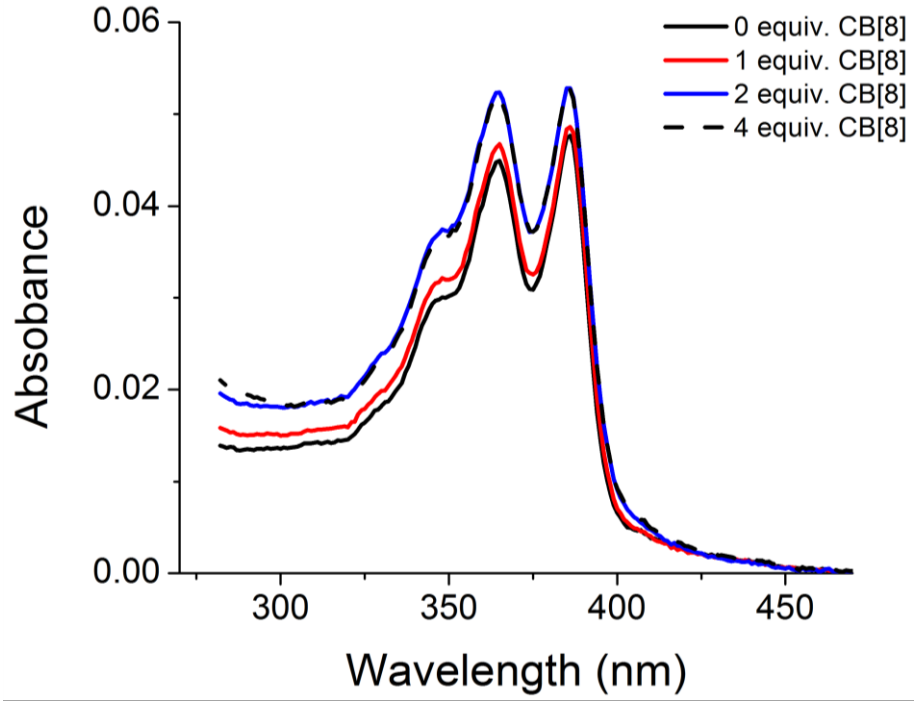


Figure S6.9: Absorption spectra of **NDI5** in 0.1% TFA in water with equimolar titrations of CB[8].

S7: Additional time-resolved fluorescence data

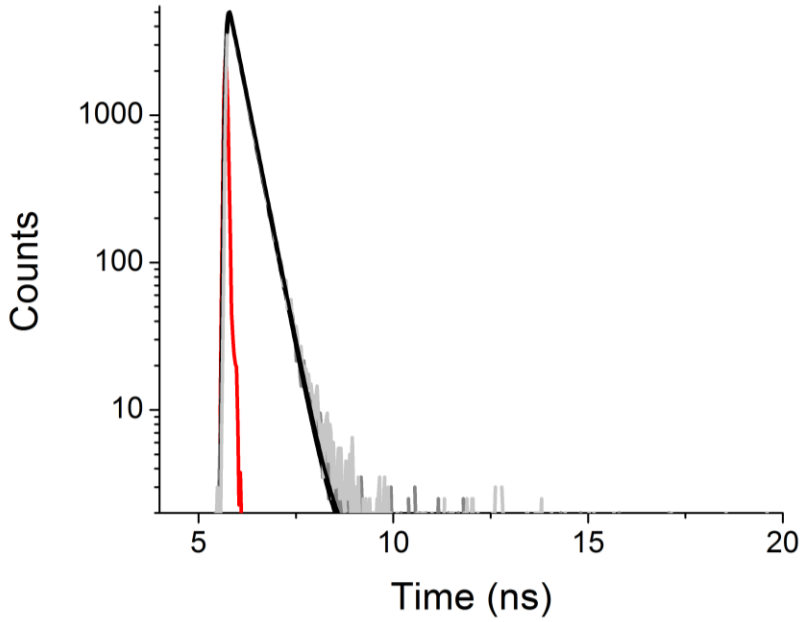


Figure S7.1: TCSPC fluorescence decay profiles of **NDI2** in 0.1% TFA in water with 0 (light grey) and 2 (grey) equivalents of CB[8], emission monitored at 415 nm. Fitted function (black lines) and the instrument response function (red lines). λ_{ex} = 375 nm.

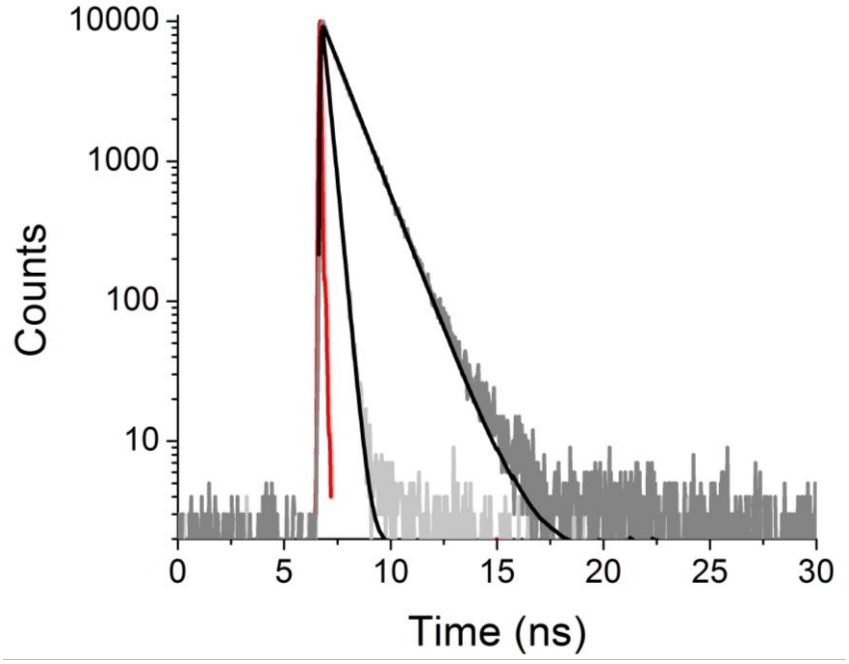


Figure S7.2: TCSPC fluorescence decay profiles of **NDI3** in 0.1% TFA in water with 0 (light grey) and 2 (grey) equivalents of CB[8] emission monitored at 415 nm. Fitted function (black lines) and the instrument response function (red lines). λ_{ex} = 375 nm.

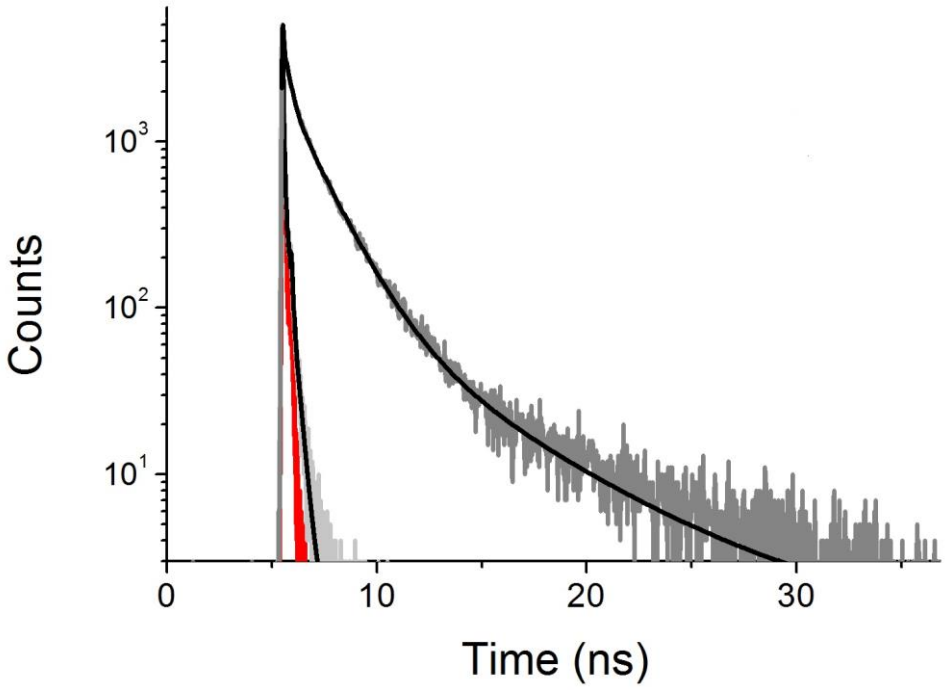


Figure S7.3: TCSPC fluorescence decay profiles of **NDI4** in 0.1% TFA in water with 0 (light grey) and 2 (grey) equivalents of CB[8] emission monitored at 415 and 500 nm, respectively. Fitted function (black lines) and the instrument response function (red lines). λ_{ex} = 375 nm.

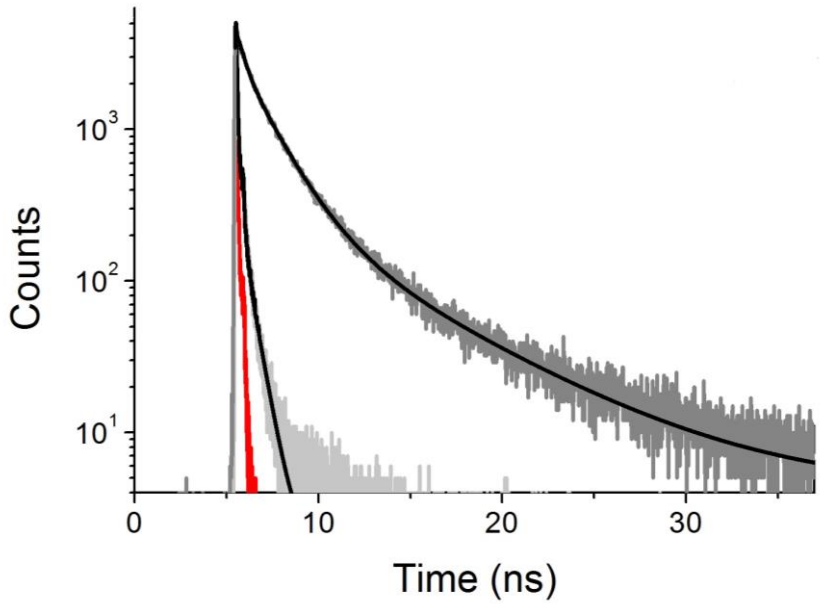


Figure S7.4: TCSPC fluorescence decay profiles of **NDI5** in 0.1% TFA in water with 0 (light grey) and 2 (grey) equivalents of CB[8] emission monitored at 415 and 500 nm, respectively. Fitted function (black lines) and the instrument response function (red lines). λ_{ex} = 375 nm.

S8: References

[1] W. H. Melhuish, *J. Phys. Chem.* 1961, 65, 229−235.

[2] R. P. Cox, H. F. Higginbotham, B. A. Graystone, S. Sandanayake, S. J. Langford and T. D. M. Bell, *Chem. Phys. Lett.*, 2012, 521, 59-63.

[3] S. Ulrich, A. Petitjean and J.-M. Lehn, *Eur. J. Inorg. Chem.*, 2010, 1913-1928.

[4] A. Sahana, A. Banerjee, S. Lohar, S. Panja, S. Mukhopadhyay, J. Matalobos and D. Das, *Chem. Commun.*, 2013, 49, 7231-7233.