Supporting Information for:

Modulating the Optical Properties of BODIPY Dyes by Noncovalent Dimerization within a Flexible Coordination Cage

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1. Materials and methods

All commercial chemicals were used as received unless stated otherwise. Solvents were dried according to standard procedures. Synthesis was carried out in oven-dried glassware. NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer, a Bruker Avance III HD 500 MHz spectrometer, or a Bruker Avance III 800 MHz spectrometer. Chemical shifts (δ) are given in ppm relative to residual proton solvent resonances (4.79 ppm for D2O and 7.26 ppm for CDCl3). 1H DOSY measurements were performed on a Bruker Avance III 500 MHz spectrometer with temperature and gradient calibration prior to the measurements (the diffusion coefficient of the solvent was used as a calibration standard). A constant temperature of 298 K was maintained during all NMR measurements unless stated otherwise. Solution and solid-state UV–vis absorption spectra were recorded with a Shimadzu UV-2700 or a UV-3600 spectrophotometer. Emission and excitation spectra were recorded with a Shimadzu spectrofluorophotometer RF-5301 PC. Fluorescence quantum yields were determined on a Quantaurus-QY Absolute PL quantum yield spectrometer. Experimental details about the time-resolved fluorescence and absorbance spectroscopy can be found in Section 10. For details on the X-ray data collection and refinement, see Section 13.
2. Synthesis of cage 1

Coordination cage 1 was synthesized based on a reported literature procedure.\textsuperscript{1}

\textsuperscript{1}H NMR (500 MHz, D$_2$O): $\delta = 9.12$ (s, 8H, 1$_4$), 8.83 (s, 4H, 1$_1$), 7.75 (s, 4H, 1$_8$), 7.73 (s, 4H, 1$_3$), 7.71 (s, 8H, 1$_7$), 7.66 (s, 8H, 1$_6$), 7.56 (s, 12H, 1$_{12}$-s), 3.13 (s, 24H, 1$_{11}$), 2.84–2.66 (m, 72H, 1$_{12}$).

\textsuperscript{13}C NMR (100 MHz, D$_2$O): $\delta = 138.04$ (1$_9$), 137.76 (1$_{10}$), 137.51 (1$_4$), 137.26 (1$_1$), 128.73 (1$_{12}$-s), 120.74 (1$_6$), 120.51 (1$_3$), 114.78 (1$_8$), 113.09 (1$_7$), 62.52 (1$_{11}$), 50.29 (1$_{12}$), 50.24 (1$_{12}$), 50.02 (1$_{12}$).

\textbf{Figure S1.} \textsuperscript{1}H NMR spectrum of 1 (500 MHz, D$_2$O, 298 K).
Figure S2. $^{13}$C NMR spectrum of 1 (100 MHz, D$_2$O, 298 K).
3. Synthesis and characterization of BODIPY dyes 2, 3, and 4

BODIPY 2 was synthesized based on a reported literature procedure.\textsuperscript{2}

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta = 6.05 (s, 2H, 2a), 2.57 (s, 3H, 2b), 2.52 (s, 6H, 2i), 2.41 (s, 6H, 2j)\).

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta = 153.73 (25), 141.57 (26), 141.14 (28), 132.22 (27), 121.36 (24), 17.43 (22), 16.49 (23), 14.55 (21)\).

\textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}): \(\delta = -147.42 (q)\).

\textbf{Figure S3.} \textsuperscript{1}H NMR spectrum of 2 (400 MHz, CDCl\textsubscript{3}, 298 K).
Figure S4. $^{13}$C NMR spectrum of 2 (100 MHz, CDCl$_3$, 298 K).

Figure S5. $^{19}$F NMR spectrum of 2 (376 MHz, CDCl$_3$, 298 K).
BODIPY 3 was obtained as a byproduct in the synthesis of 8-acetoxymethyl-1,2,3,5,6,7-hexamethyl pyromethene fluoroborate. Specifically, acetoxyacetyl chloride (0.87 mL; 8.1 mmol; 1.2 eq) was slowly added to a solution of 2,3,4-trimethyl-1H-pyrrole (1.478 g; 13.5 mmol; 2.0 eq) in dry CH2Cl2 (6 mL). During the addition, the solution warmed up and turned deep-red. Then, the mixture was refluxed for 1 h, cooled down, and poured onto n-hexane (100 mL). The solvent was evaporated to afford a deep-red solid. The solid was redissolved in dry CH2Cl2 (70 mL) containing 6.8 mL (39 mmol) of diisopropylethylamine. After having been stirred for 10 min at room temperature, BF3·OEt2 (7.2 mL; 58 mmol) was added dropwise and the solution was stirred for 1 h at the same temperature, turning violet. Then, the reaction was discontinued and the mixture was washed with a saturated aqueous solution of NaHCO3 (3 × 100 mL) and dried over Na2SO4. The solvent was evaporated and the resulting solid was purified by column chromatography (CH2Cl2/petroleum ether 1/1). BODIPY 3 was isolated as a dark-purple solid. Yield: 167 mg (0.55 mmol, 8%).

The peaks in the NMR spectra were assigned by analyzing 2D NMR spectra (not shown).

1H NMR (400 MHz, CDCl3): δ = 10.60 (s, 1H, 33), 2.49 (s, 6H, 31), 2.02 (s, 6H, 32), 1.91 (s, 6H, 34).

13C NMR (100 MHz, CDCl3): δ = 194.19 (33), 157.12 (35), 137.07 (36), 134.87 (38), 128.06 (37), 127.34 (39), 13.22 (31), 13.18 (32), 9.11 (34).

19F NMR (376 MHz, CDCl3): δ = -146.57 (q).

Figure S6. 1H NMR spectrum of 3 (400 MHz, CDCl3, 298 K).
Figure S7. $^{13}$C NMR spectrum of 3 (100 MHz, CDCl$_3$, 298 K).

Figure S8. $^{19}$F NMR spectrum of 3 (376 MHz, CDCl$_3$, 298 K).
Figure S9. ORTEP representation of the X-ray structure of BODIPY 3 (thermal ellipsoids at a 50% probability level). C, gray; N, blue; O, red; B, yellow; F, green (note that the X-ray structures of BODIPYs 2 and 4 have been reported previously)."

BODIPY 4 was synthesized based on a reported literature procedure.  

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 6.15\) (s, 2H, 4\(\text{a}\)), 2.54 (s, 6H, 4\(\text{i}\)), 2.33–2.25 (m, 6H, 4\(\text{z}\)).  

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 158.84\) (4\(\text{s}\)), 143.14 (4\(\text{e}\)), 131.3 (4\(\text{z}\)), 124.41 (4\(\text{g}\)), 123.71 (4\(\text{i}\)), 120.98 (4\(\text{a}\)), 15.87 (4\(\text{b}\)), 15.00 (4\(\text{i}\)).  

\(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta = -53.51\) (t, 3F, 4\(\text{CF}\_3\)), -146.86 (q, 2F, 4\(\text{BF}\_2\)).

Figure S10. \(^1\)H NMR spectrum of 4 (400 MHz, CDCl\(_3\), 298 K).
Figure S11. $^{13}$C NMR spectrum of 4 (100 MHz, CDCl$_3$, 298 K).

Figure S12. Full-range (left) and partial (right) $^{19}$F NMR spectrum of 4 (376 MHz, CDCl$_3$, 298 K).
4. Encapsulation of BODIPYs 2, 3, and 4 within cage 1

*General procedure for encapsulation:* Cage 1 (9.0 mg, 2.8 µmol) was dissolved in D$_2$O (0.7 mL). The resulting colorless solution was added to an excess (>5 eq) of solid 2, 3, or 4 (none of which is soluble in water) and the resulting suspensions were stirred overnight in the dark at ambient temperature. Then, the undissolved solids were removed by several cycles of centrifugation, resulting in clear, intensely colored solutions. Stirring for a longer time, heating, and applying sonication did not increase the encapsulation yields. The resulting solutions were stable in the dark at ambient temperature for at least several months (verified by NMR and UV–vis absorption spectroscopy).

The intense colorization of the aqueous solutions of 1 in the visible area allowed us to follow the uptake of each BODIPY dye by the cage over time. To this end, aliquots from the suspensions were taken at various times, subjected to repeated centrifugations, and analyzed by UV–vis absorption spectroscopy. Representative UV–vis spectra are shown in Figure S13. Based on the results replotted in Figure S14, we concluded that the uptake of all the BODIPY dyes is complete within ~10 h, with minor differences between dyes 2, 3, and 4.

![Figure S13](image1.png)

**Figure S13.** Uptake of 2 (A), 3 (B), and 4 (C) by cage 1 over time followed by UV–vis absorption spectroscopy.

![Figure S14](image2.png)

**Figure S14.** Absolute (A) and normalized (B) profiles of the uptake of BODIPYs 2, 3, and 4 by cage 1. Absorbance was followed at 480 nm, 519 nm, and 523 nm for 2, 3, and 4, respectively.
5. NMR characterization of inclusion complex $2_2 \subset 1$

Inclusion complex $2_2 \subset 1$ was obtained in ~50% yield as determined by $^1$H NMR spectroscopy. To help assign peaks due to 1 vs 2, as-prepared $2_2 \subset 1$ was treated with extra free 1 (see Figure S16).

$^1$H NMR (500 MHz, D$_2$O): $\delta$ = 9.55 (s, 4H, 1$_4$), 9.29 (s, 4H, 1$_4'$), 8.81 (s, 4H, 1$_{1-1'}$), 8.31 (s, 2H, 1$_8$), 8.07 (s, 4H, 1$_7$), 8.00 (s, 2H, 1$_3$), 7.91 (br, 4H, 1$_6$), 7.78 (s, 2H, 1$_2$), 7.74–7.66 (m, 8H, 1$_{5,3-5'}$), 7.58 (s, 2H, 1$_2'$), 7.53 (s, 4H, 1$_5'$), 7.43 (s, 4H, 1$_7'$), 7.18 (br, 4H, 1$_9$), 5.59 (s, 4H, 2$_4$), 3.09 (s, 24H, 2$_6$), 2.83–2.54 (m, 72H, 1$_{12}$), 1.87 (br, 12H, 2$_1$), 0.62 (s, 12H, 2$_2$), 0.26 (s, 6H, 2$_3$).

$^{13}$C NMR (125 MHz, D$_2$O): $\delta$ = 151.98 (2$_5$), 140.54 (1$_9$/9'/10'/10'/2$_6$), 139.34 (1$_9$/9'/10'/10'/2$_a$), 138.56 (2$_7$), 137.45 (1$_9$/9'/10'/10'/2$_b$), 137.62 (1$_9$/9'/10'/10'/2$_c$), 137.41 (1$_9$/9'/10'/10'/2$_d$), 137.21 (1$_4-4'$), 137.04 (1$_{11'}$), 136.66 (1$_{11}$), 130.34 (2$_8$), 129.71 (1$_b$), 129.36 (1$_2$), 128.71 (1$_2'/3'$), 121.16 (2$_a$), 120.36 (1$_3$), 120.07 (1$_d$), 119.81 (1$_p$), 119.42 (1$_y$), 111.43 (1$_b$), 110.68 (1$_r$), 110.00 (1$_w$), 109.24 (1$_r'$), 102.61 (1$_{12}$), 50.43–49.91 (1$_{11}$), 14.92 (2$_2$), 13.53 (2$_1$), 13.31 (2$_1$).

$^{19}$F NMR (470 MHz, D$_2$O): $\delta$ = (-142.72)–(-143.17) (m, 2F, 2$_{BF}$), -144.70 (br, 2F, 2$_{BF}$).

$^1$H DOSY NMR (500 MHz, D$_2$O): $D = 0.15 \times 10^{-5}$ cm$^2$/s.

**Figure S15.** $^1$H NMR spectrum of $2_2 \subset 1$ (500 MHz, D$_2$O, 298 K).
Figure S16. $^1$H NMR spectrum of as-prepared 2⊂1 (in the presence of free cage 1, which always remains partially unfilled) (bottom; red), after the addition of an extra 1 equiv of free 1 (center; green), and after the addition of an extra 2 equiv of free 1 (i.e., a total of 3 equiv of 1) (top; dark-blue) (400 MHz, D$_2$O, 298 K).
Figure S17. $^{13}$C NMR spectrum of $2\subset 1$ (125 MHz, D$_2$O, 298 K).

Figure S18. $^{19}$F NMR spectrum of $2\subset 1$ (470 MHz, D$_2$O, 298 K).
Figure S19. $^1$H DOSY NMR spectrum of $2_2$<1 (500 MHz, D$_2$O, 298 K).

Figure S20. Partial $^1$H–$^1$H COSY NMR spectrum of $2_2$<1 (500 MHz, D$_2$O, 298 K).
Figure S21. $^1$H–$^{13}$C HSQC NMR spectrum of 2⊂1 (500 MHz, D$_2$O, 298 K).

Figure S22. Partial $^1$H–$^{13}$C HSQC NMR spectrum of 2⊂1 (500 MHz, D$_2$O, 298 K).
Figure S23. $^1$H–$^{13}$C HMBC NMR spectrum of $2_2\subset 1$ (500 MHz, D$_2$O, 298 K).

Figure S24. Partial $^1$H–$^{13}$C HMBC NMR spectrum of $2_2\subset 1$ (500 MHz, D$_2$O, 298 K).
Figure S25. $^1$H–$^1$H NOESY NMR spectrum of $2\subset 1$ (500 MHz, D$_2$O, 298 K).

Figure S26. Partial $^1$H–$^1$H NOESY NMR spectrum of $2\subset 1$ showing nuclear Overhauser (nOe) correlations between 1 and 2 (500 MHz, D$_2$O, 298 K).
Figure S27. Partial $^1$H–$^1$H NOESY NMR spectrum of 2⊂1 showing nOe correlations between 1 and 2 and between two co-encapsulated molecules of 2 (500 MHz, D$_2$O, 298 K).

Figure S28. Partial $^1$H–$^{19}$F HOESY NMR spectrum of 2⊂1 (500 MHz, D$_2$O, 298 K).
6. NMR characterization of inclusion complex 3$_2$$\subset$1

Inclusion complex 3$_2$$\subset$1 was obtained in a quantitative yield, as determined by $^1$H NMR spectroscopy.

$^1$H NMR (500 MHz, D$_2$O): $\delta$ = 9.71 (s, 4H, 1$_4$), 9.48 (s, 4H, 1$_4'$), 8.84 (s, 2H, 1$_1$), 8.80 (s, 2H, 1$_1'$), 8.57 (s, 2H, 3$_5$), 8.56 (s, 2H, 1$_5$), 8.08 (s, 2H, 1$_7$), 8.05 (s, 2H, 1$_7'$), 7.97 (s, 4H, 1$_8$), 7.81 (s, 2H, 1$_8'$), 7.73 (s, 2H, 1$_9$), 7.62 (s, 4H, 1$_5$), 7.59 (s, 2H, 1$_2$), 7.51 (s, 4H, 1$_5'$), 7.36 (br, 4H, 1$_6'$), 3.09 (s, 24H, 1$_{11}$), 2.84–2.52 (m, 72H, 1$_{12}$), 2.24 (br, 12H, 3$_4$), 1.58 (s, 12H, 3$_4'$), -0.06 (s, 12H, 3$_2$).

$^{13}$C NMR (125 MHz, D$_2$O): $\delta$ = 195.70 (3$_3$), 155.65 (3$_4$), 138.97 (1$_9$+9'/3), 138.24 (1$_9$+9'/3), 137.76 (1$_4$), 137.44 (1$_4'$+1'+10), 136.80 (1$_{10}$), 136.58 (1$_1$), 136.09 (1$_9$+9'/3), 132.19 (3$_8$), 129.56 (1$_5$), 128.63 (1$_2$), 128.54 (1$_5$'), 126.95 (3$_4$), 126.38 (3), 120.25 (1$_3$), 119.24 (1$_{6'}$), 119.16 (1$_7$'), 111.92 (1$_8$), 110.68 (1$_8'$), 109.57 (1$_7$), 107.62 (1$_{10}$), 62.66 (1$_{11}$), 50.41 (1$_{12}$), 50.22 (1$_{12}$), 12.14 (3), 10.37 (3), 7.90 (3).

$^{19}$F NMR (470 MHz, D$_2$O): $\delta$ = (-143.0)–(-144.0) (m, 2F, 3), -145.0 (br, 2F, 3).

$^1$H DOSY NMR (500 MHz, D$_2$O): $D = 0.15 \times 10^{-5}$ cm$^2$/s.

Figure S29. $^1$H NMR spectrum of 3$_2$$\subset$1 (500 MHz, D$_2$O, 298 K).
**Figure S30.** $^{13}$C NMR spectrum of $3\subset 1$ (125 MHz, D$_2$O, 298 K).

**Figure S31.** $^{19}$F NMR spectrum of $3\subset 1$ (470 MHz, D$_2$O, 298 K).
Figure S22. $^1$H DOSY NMR spectrum of 3$_2$\(\subset\)1 (500 MHz, D$_2$O, 298 K).

Figure S33. $^1$H–$^1$H COSY NMR spectrum of 3$_2$\(\subset\)1 (500 MHz, D$_2$O, 298 K).
Figure S34. Partial $^1$H–$^1$H COSY NMR spectrum of 3⊂1 (500 MHz, D₂O, 298 K).

Figure S35. $^1$H–$^{13}$C HSQC NMR spectrum of 3⊂1 (500 MHz, D₂O, 298 K).
Figure S36. Partial $^1$H–$^{13}$C HSQC NMR spectrum of 3$_2$$<_1$ (500 MHz, D$_2$O, 298 K).

Figure S37. $^1$H–$^{13}$C HMBC NMR spectrum of 3$_2$$<_1$ (500 MHz, D$_2$O, 298 K).
Figure S38. Partial $^1$H–$^{13}$C HMBC NMR spectrum of 3⊂1 (500 MHz, D$_2$O, 298 K).
Figure S39. $^1$H–$^1$H NOESY NMR spectrum of $3_2$$\subset$$^1$ (500 MHz, D$_2$O, 298 K).

Figure S40. Partial $^1$H–$^1$H NOESY NMR spectrum of $3_2$$\subset$$^1$ showing nOe correlations between $^1$ and 3 (500 MHz, D$_2$O, 298 K).
Figure S41. Partial $^1$H–$^1$H NOESY NMR spectrum of $3_{3} \subset 1$ showing nOe correlations between 1 and 3 and between two co-encapsulated molecules of 3 (500 MHz, D$_2$O, 298 K).
7. NMR characterization of inclusion complex $4_2 \subset 1$

Inclusion complex $4_2 \subset 1$ was obtained in ~62% yield, as determined by UV–vis absorption spectroscopy (see Section 9). The signals in the NMR spectra of $4_2 \subset 1$ were significantly broader than those of the other two inclusion complexes, which made the analysis of $4_2 \subset 1$ using 2D NMR methods challenging.

$^1$H NMR (500 MHz, D$_2$O): $\delta = 9.59$ (s), 9.34 (s), 9.13–9.05 (br), 8.15–7.77 (br), 5.98 (s), 3.31 (s), 3.29 (s), 2.97 (s), 2.87 (s), 1.62 (br), 1.01 (s).

$^{13}$C NMR (125 MHz, D$_2$O): $\delta = 137.81$, 137.39, 129.11, 128.80, 124.63, 121.87, 120.97, 119.66, 119.14, 109.27, 62.60, 50.27, 14.06.

$^{19}$F NMR (470 MHz, D$_2$O): $\delta = -55.3$ (s, 6F, $3_{CF3}$) (-138.3)–(-143.3) (m, 2F, $3_{BF2}$), -145.0 (m, 2F, $3_{BF2}$).

Figure S42. $^1$H NMR spectrum of $4_2 \subset 1$ (500 MHz, D$_2$O, 318 K). Note that the spectrum was recorded at 318 K; the peaks at room temperature were significantly broader.
Figure S43. $^{13}$C NMR spectrum of 4$_2$□1 (125 MHz, D$_2$O, 298 K).

Figure S44. $^{19}$F NMR spectrum of 4$_2$□1 (470 MHz, D$_2$O, 298 K).
8. X-ray crystallography of complexes 2⊂1, 3⊂1, and 4⊂1

Table S1 lists the structural parameters of cage 1 (free and encapsulating BODIPYs 2–4). Crystals of inclusion complexes 2⊂1 and 4⊂1 contained a single type of species. Single crystals of 3⊂1 contained two alternating inclusion complexes with slightly different conformations.

| Species | Pd_{ax}–Pd_{ax} distance | Pd_{eq}–Pd_{eq} distance | Angle at Pd_{ax} |
|---------|--------------------------|--------------------------|------------------|
| 1       | 16.86 Å                  | 18.23 Å                  | 88.59°           |
| 2⊂1     | 18.44 Å                  | 16.84 Å                  | 76.38°           |
| 3⊂1     | 18.16 Å / 18.59 Å        | 17.09 Å / 16.70 Å        | 78.65° / 75.37°  |
| 4⊂1     | 18.42 Å                  | 16.91 Å                  | 76.89°           |

Table S1. Structural parameters for empty 1 and 1 encapsulating BODIPYs 2–4. Pd_{ax} and Pd_{eq} denote axial and equatorial palladium nodes, respectively; the Pd_{ax}–Pd_{ax} distance is defined as the distance between two axial palladium nodes. The Pd_{eq}–Pd_{eq} distance is defined as the average distance between two opposite equatorial palladium nodes of the cage. The angle at Pd_{ax} is defined as angle between two Tlm ligand planes at the axial position. All calculations of distances and angles were performed using Mercury 4.2.0 software.

Table S2 lists the structural parameters of BODIPYs 2–4 within the crystals of pure BODIPYs and the corresponding 2:1 inclusion complexes with cage 1.

| Species | Plane-to-plane distance | Center-to-center distance | Slip angle |
|---------|-------------------------|--------------------------|------------|
| 2⊂1     | 3.58 Å                  | 4.68 Å                   | 65.35°     |
| 2∞      | 3.52 Å                  | 4.98 Å                   | 65.05°     |
| 3⊂1     | 3.59 Å / 3.62 Å         | 4.23 Å / 4.34 Å          | 69.65° / 73.45° |
| 3∞      | 3.57 Å                  | 4.30 Å                   | 71.87°     |
| 4⊂1     | 3.81 Å                  | 4.83 Å                   | 64.12°     |
| 4∞      | 3.71 Å                  | 6.49 Å                   | 37.68°     |

Table S2. Structural parameters for aggregated BODIPYs 2, 3, and 4 within single crystals and inside cage 1. For the calculation of plane-to-plane distances between two neighboring BODIPY units, individual planes were defined and calculated as surfaces based on the central C_{3}BN_{2} ring of each BODIPY. For calculating the center-to-center distances, centroids within the same C_{3}BN_{2} core units were calculated. The transition dipole moment of the S_{1}←S_{0} absorption is polarized along the long axis of the BODIPY chromophore. Thus, the slip angle, θ, between the two dipole moments in a closely packed dimer was calculated as the inner angle of the triangle C1–centroid1–centroid2 (see the main text, Figure 1c, bottom). All calculations of distances, angles, centroids, and planes were performed using Mercury 4.2.0 software.
Figure S45. ORTEP representation of the X-ray structure of inclusion complex 2⊂1 (thermal ellipsoids at a 50% probability level). Hydrogens, anions, and solvent molecules were eliminated for clarity. Pd, yellow; C gray; N, blue; O, red; B, brown; F, green.
Figure S46. ORTEP representation of the X-ray structure of the first conformer of inclusion complex $3_2 \subset 1$ (thermal ellipsoids at a 50% probability level). Hydrogens, anions, and solvent molecules were eliminated for clarity. Pd, yellow; C gray; N, blue; O, red; B, brown; F, green.
Figure S47. ORTEP representation of the X-ray structure of the second conformer of inclusion complex $3_2 \subset 1$ (thermal ellipsoids at a 50% probability level). Hydrogens, anions, and solvent molecules were eliminated for clarity. Pd, yellow; C gray; N, blue; O, red; B, brown; F, green.
Figure S48. ORTEP representation of the X-ray structure of inclusion complex 4⊂1 (thermal ellipsoids at a 50% probability level). Hydrogens, anions, and solvent molecules were eliminated for clarity. Pd, yellow; C gray; N, blue; B, brown; F, green.

Figure S49. Comparison of the X-ray structures of 2⊂1, 3⊂1, and 4⊂1 (note that whereas the X-ray structures of 2⊂1 and 4⊂1 contained only one type of species, that of 3⊂1 featured two slightly different conformations (in a 1:1 ratio). Only one of them in shown here; for the other conformation, see the CIF file).
9. Steady-state optical properties of 2–4 and their inclusion complexes

UV–vis absorption measurements were carried out on 0.04 mM solutions of inclusion complexes (the concentration in terms of cage units) at ambient temperature. The solution of free cage 1 is practically transparent in the visible range, with an absorption onset at ~380 nm. BODIPY 2 dissolved in MeCN (note that 2–4 are all insoluble in water) exhibits optical behavior typical of classical BODIPY dyes, namely, a sharp absorption band in the visible range centered at 491 nm (corresponding to the S₁←S₀ transition) with a blue-shifted vibronic shoulder (see Figure S50A). A minor, broader absorption seen centered at 354 nm corresponds to the S₂←S₀ transition. Fluorophore 2 exhibits an intense green fluorescence with the emission band mirroring the absorption band. The emission band is centered at 502 nm, giving rise to a small Stokes shift (11 nm) characteristic of BODIPY dyes. BODIPY 3 has an intensive violet color, with a main absorbance band at 533 nm. The fluorescence quantum yield of 3 is much lower than that of 2 due to quenching effects associated with the CHO group. The excitation spectrum recorded on a solution of 3 does not follow its absorption spectrum (excitation maximum = 517 nm), with the emission band centered at the same wavelength as the absorption band (533 nm). We hypothesize that the excitation spectrum may originate from a minor yet highly emissive species, such as a rotamer or protonated 3. BODIPY 4 is red-purple with the main absorbance band at 548 nm. As reported previously, 4 it has a low fluorescence quantum yield, with a weak emission band at 595 nm. Note that the absorbance bands of 3 and 4 are significantly broader than for 2, which is likely due to the bulkiness of the substituents at the meso position (CHO and CF₃).

The absorption maxima of inclusion complexes 2⊂1, 3⊂1, and 4⊂1 in water are blue-shifted with respect to the corresponding non-encapsulated dyes in MeCN. For 2⊂1, the main absorbance band is centered at 480 nm (Δ-abs = 11 nm). The fluorescence is largely quenched and appears yellow, with the main emission band red-shifted to 544 nm (giving rise to a Stokes shift of 64 nm; compare with 11 nm for free 2 in MeCN). The hypsochromic shift of the main absorption band and the decreased fluorescence quantum yield are well-known characteristics of the H-type dimers of chromophores stacked closely in an antiparallel fashion. These characteristics can be described by Kasha’s model of exciton coupling in molecular dimers. 5 For 3⊂1, the absorbance band is centered at 520 nm (Δ-abs = 13 nm), with a largely quenched fluorescence (emission maximum = 539 nm). The absorbance band of 4⊂1 is centered at 523 nm. The excitation spectra of 4⊂1 does not follow the absorbance spectra, with the excitation maximum centered at 562 nm.

![Normalized absorption, emission, and excitation spectra](image)

**Figure S50.** Normalized absorption, emission, and excitation spectra of (A) 2 (λexc = 460 nm), (B) 3 (λexc = 500 nm), and (C) 4 (λexc = 530 nm), all in MeCN. The wavelengths of maximum absorption and emission are denoted in black and red, respectively. The wavelengths of maximum excitation are very similar to those of the absorption spectra, except for (B), where λ_max = 517 nm (note that the fluorescence quantum yield of 3 is low; the excitation and emission spectra could originate from a highly emissive rotamer or another species, such as protonated 3).
Figure S51. Normalized absorption, emission, and excitation spectra of (A) \( 2_2 \subset 1 \) (\( \lambda_{\text{exc}} = 460 \text{ nm} \)), (B) \( 3_2 \subset 1 \) (\( \lambda_{\text{exc}} = 500 \text{ nm} \)), and (C) \( 4_2 \subset 1 \) (\( \lambda_{\text{exc}} = 530 \text{ nm} \)), all in \( \text{H}_2\text{O} \). The wavelengths of maximum absorption and emission are denoted in black and red, respectively. The wavelengths of maximum excitation are very similar to those of the absorption spectra, except for (C), where \( \lambda_{\text{max}} = 562 \text{ nm} \).

Addition of MeCN to an aqueous solution of \( 2_2 \subset 1 \) instantly results in a significant (fluorescence) color change of the solution, as shown below:

![Image](https://example.com/image.png)

Figure S52. The instantaneous emission color change of an aqueous solution of \( 2_2 \subset 1 \) upon the addition of MeCN (\( \lambda_{\text{exc}} = 365 \text{ nm} \)).

To investigate this process in more detail, we followed the process by UV–vis absorption and fluorescence spectroscopies. We tested several organic solvents, in which BODIPYs 2–4 are readily soluble (MeCN, acetone, DMF, 1,4-dioxane, DMSO, and MeOH). In a typical experiment, a 0.04 mM solution of \( 2_2 \subset 1 \) in 2 mL of water (the concentration in terms of cage units) was treated with 100 \( \mu \text{L} \) aliquots of an organic solvent. After the addition of each aliquot, the solution was thoroughly mixed and the spectrum was recorded. The aliquots were added until no further changes in the spectra (other than those due to dilution) were observed. We verified that in all the experiments, all the species (1, 2, and \( 2_2 \subset 1 \)) remained dissolved in solution.

The release of 2 from \( 2_2 \subset 1 \) upon the addition of MeCN was accompanied by the appearance of a sharp, intense absorption band, characteristic of monomeric BODIPYs in solution (see Figure S53A). In addition, fluorescence spectroscopy showed a rapid increase in the emission intensity (Figure S53C).

Concentration-corrected spectra show that the absorption coefficient of 2 within 1, \( \varepsilon_2' \), is substantially smaller than that of free 2 in solution (\( \varepsilon_2 \); specifically, we found that \( \varepsilon_2' \approx 0.45 \varepsilon_2 \)). In other words, the release of 2 from the cage leads not only to a bathochromic shift but also to a substantial increase in the absorption intensity. Provided that the final solution contains only monomeric 2 in solution (i.e., no encapsulated 2), we can calculate, based on the molar absorption coefficient of 2 (~80,000 L mol\(^{-1}\) cm\(^{-1}\))\(^4\), the percentage of 1
encapsulating the noncovalent dimer of 2. The result of this calculation (~50%) is in a very good agreement with the encapsulation efficiency determined by $^1$H NMR.

Next, we investigated the release of 2 from $2_2 \subset 1$ using other organic solvents. As Figure S53B shows, the release commences only after a certain volume percentage of a polar organic solvent has been added. We found that MeCN, dioxane, acetone, and DMF were similarly efficient in releasing the dye from the cage. However, higher volume fractions of DMSO and MeOH had to be added to reach the same level of release. In all cases, the final absorption spectra were identical to those of free 2 in the corresponding organic solvent, indicating that 2 was released from the cage in a quantitative fashion.

The same experiments were repeated with BODIPY 4 and inclusion complex $4_2 \subset 1$ (Figures S53D–F). The results were analogous, except that, in contrast to BODIPY 2, the fluorescence emission of 4 is higher inside the cage than in organic solution, resulting in decreased fluorescence emission upon the addition of an organic solvent (see Figure S53F). Given the molar extinction coefficient of free 4, $\varepsilon_4 \approx 45,000$ L mol$^{-1}$ cm$^{-1}$, the percentage of filled 1 at the onset of the experiment was determined as 62%.

**Figure S53.** (A) Changes in the absorption spectrum of $2_2 \subset 1$ in H$_2$O upon the gradual addition of MeCN (concentration-corrected). We found that the extinction coefficient of 2 within 1, $\alpha(2_2 \subset 1)$, amounts to roughly $0.45 \times \alpha(2)$. (B) Plots of concentration-corrected absorbance (at the wavelength of maximum absorption of free 2 in a given solvent) as a function of the volume of organic solvent added. (C) Changes in the emission spectrum ($\lambda_{exc} = 460$ nm) of $2_2 \subset 1$ in H$_2$O upon the gradual addition of MeCN (concentration-corrected). (D) Changes in the absorption spectrum of $4_2 \subset 1$ in H$_2$O upon the gradual addition of MeCN (concentration-corrected). (E) Plots of concentration-corrected absorbance (at the wavelength of the maximum absorption of free 4 in a given solvent) as a function of the volume of organic solvent added. (F) Changes in the emission spectrum ($\lambda_{exc} = 530$ nm) of $4_2 \subset 1$ in H$_2$O upon the gradual addition of MeCN (concentration-corrected).
Samples for solid-state UV–vis absorption spectra were prepared by dropcasting MeCN solutions of BODIPYs 2–4 and aqueous solutions of inclusion complexes 2⊂1, 3⊂1, and 4⊂1 on glass slides, followed by solvent evaporation. For solution-state spectra of free 2, 3, and 4, MeCN was used as the solvent. Samples of aggregates of 2, 3, and 4 were prepared by diluting MeCN solutions of the compounds with 49 volumes of H2O; the spectra were recorded ~30 s after the addition of H2O. For solid-state spectra of 2⊂1 and 4⊂1, note that the samples contain residual unfilled cages (~1 equiv of free 1 for 2⊂1 and ~0.6 equiv of free 1 for 4⊂1).

**Figure S54.** (A) Comparison of normalized solution UV–vis absorption spectra of 2 (MeCN) and 2⊂1 (H2O). (B) Comparison of normalized solution UV–vis absorption spectra of 3 (MeCN) and 3⊂1 (H2O). (C) Comparison of normalized solution UV–vis absorption spectra of 4 (MeCN) and 4⊂1 (H2O).

**Figure S55.** (A) Comparison of normalized solution (MeCN) and solid-state UV–vis absorption spectra of 2. (Note that due to the formation of large crystals as opposed to continuous films, the solid-state spectrum of 2 is featureless and has not been normalized.) (B) Comparison of normalized solution (MeCN) and solid-state UV–vis absorption spectra of 3. (C) Comparison of normalized solution (MeCN) and solid-state UV–vis absorption spectra of 4.

**Figure S56.** (A) Comparison of normalized UV–vis absorption spectra of 2⊂1 (H2O) and aggregated 2 (H2O/MeCN, v/v = 49:1). (B) Comparison of normalized UV–vis absorption spectra of 3⊂1 (H2O) and aggregated 3 (H2O/MeCN, v/v = 49:1). (C) Comparison of normalized UV–vis absorption spectra of 4⊂1 (H2O) and aggregated 4 (H2O/MeCN, v/v = 49:1).
Figure S57. (A) Comparison of the solid-state UV–vis absorption spectrum of 2 and the solution spectrum of aggregated 2 (H₂O/MeCN, v/v = 49:1; normalized). (Note that due to the formation of large crystals as opposed to continuous films, the solid-state spectrum of 2 is featureless and has not been normalized.) (B) Comparison of the solid-state UV–vis absorption spectrum of 3 and the solution spectrum of aggregated 3 (H₂O/MeCN, v/v = 49:1) (both normalized). (D) Comparison of the solid-state UV–vis absorption spectrum of 3 and the solution spectrum of aggregated 3 (H₂O/MeCN, v/v = 49:1) (both normalized).

Figure S58. (A) Comparison of normalized solution (H₂O) and solid-state UV–vis absorption spectra of 2⊂1. (B) Comparison of normalized solution (H₂O) and solid-state UV–vis absorption spectra of 3⊂1. (C) Comparison of normalized solution (H₂O) and solid-state UV–vis absorption spectra of 4⊂1.

Figure S59. (A) Comparison of normalized UV–vis absorption spectra of free (MeCN) and aggregated (H₂O/MeCN, v/v = 49:1) 2. (B) Comparison of normalized UV–vis absorption spectra of free (MeCN) and aggregated (H₂O/MeCN, v/v = 49:1) 3. (C) Comparison of normalized UV–vis absorption spectra of free (MeCN) and aggregated (H₂O/MeCN, v/v = 49:1) 4.
Figure S60. (A) Comparison of solution (MeCN; normalized) and solid-state UV–vis absorption spectra of 2. (Note that due to the formation of large crystals as opposed to continuous films, the solid-state spectrum of 2 is featureless and has not been normalized.) (B) Comparison of normalized solution (MeCN) and solid-state UV–vis absorption spectra of 3. (C) Comparison of normalized solution (MeCN) and solid-state UV–vis absorption spectra of 4.

Figure S61. (A) Comparison of solid-state UV–vis absorption spectra of $2 \subset 1$ (normalized) and 2. (Note that due to the formation of large crystals as opposed to continuous films, the solid-state spectrum of 2 is featureless and has not been normalized.) (B) Comparison of normalized solid-state UV–vis absorption spectra of 3 and $3 \subset 1$. (C) Comparison of normalized solid-state UV–vis absorption spectra of 4 and $4 \subset 1$.

10. Time-resolved optical properties of 2–4 and their inclusion complexes

For 2 and $2 \subset 1$, femtosecond transient absorption measurements were carried out on a system based on a mode-locked Ti:sapphire oscillator (Spectra Physics Mai Tai SP). The oscillator produced a train of <120 fs pulses (bandwidth ~12 nm FWHM) with a peak wavelength at 800 nm, typically of 900 mW, corresponding to ~10 nJ per pulse. The weak oscillator pulses were amplified by a chirped-pulse regenerative amplifier (CPA, Spectra Physics Spitfire Ace). The pulses were first stretched to several picoseconds, then regeneratively amplified in a Ti:sapphire cavity, pumped by a pulsed Nd:YLF laser (Spectra Physics Empower 45) operating at 1 kHz. After the pulse was amplified and recompressed, its energy was about 5 mJ in a train of 1,000 Hz pulses. An independent pump pulse was obtained by pumping an optical parametric amplifier (Spectra Physics OPA-800CF) that produces 120-fs pulses tunable from 300 nm to 3 μm. One Watt of light amplified on Spitfire was used; the output power of the OPA varied between a few μJ and tens of μJ (depending on the chosen wavelength) at 1 kHz. In the reported experiments, the pump was turned to 440 nm and the optical densities of the samples in 1 mm and 2 mm optical path length cuvettes were kept between 0.2 and 0.4 at the excitation wavelength. Spectral corrections and analyses were performed using SURFACE XPLORER Pro (Ultrafast Systems) and Origin 9.1 (OriginLab) software. The nanosecond fluorescence was measured using a LP920 flash photolysis system (Edinburgh Instruments, UK). The system was pumped by a Nd:YAG third harmonic (355 nm) driving an OPO (Spectra Physics, USA, Quanta-Ray Lab series, and GWU Lasertechnik, Germany, VersaScan-355 midband). The spectra were collected on an intensified CCD camera (i-Star, Andor, UK), where the delay was determined by gating the image intensifier.
Figure S62. (A) Time-resolved fluorescence spectra of 2 dissolved in MeCN. (B) Time-resolved fluorescence spectra of 2⊂1 in H2O (replotted from Figure 2b in the main text). (C) Decay of fluorescence of 2 and 2⊂1 at three different wavelengths.

For 3, 3⊂1, 4, and 4⊂1, the samples were excited by a frequency-tripled Nd:YAG Q-switched laser, pumping an optical parametric oscillator (Ekspla NT342/C/3/UV) with a pulse duration of 5 ns and a repetition rate of 10 Hz. The fluorescence was collected in the direction orthogonal to the laser incident beam using a 20 × 0.4 NA objective and spectrally filtered using a long pass filter onto a monochromator (Acton SpectraPro2150i), coupled to a photomultiplier (PMT) tube (Hamamatsu R10699). Transient emission measurements were recorded by a 600 MHz digital oscilloscope (LeCroy Wavesurfer 62Xs). Emission spectra were plotted by integrating over transient emission curve at each wavelength. Excitation pulse energy was measured by a pyroelectric sensor (PE9-C, Ophir Optronics). The same setup was used to acquire time-resolved spectra of 2 and 2⊂1, and results similar to those in Figure S62 were obtained.

Figure S63. (A) Time-resolved fluorescence spectra of 3 dissolved in MeCN. (B) Time-resolved fluorescence spectra of 3⊂1 in H2O. (C) Decay of fluorescence of 3 and 3⊂1 at three different wavelengths.

Figure S64. (A) Time-resolved fluorescence spectra of 4 dissolved in MeCN. (B) Time-resolved fluorescence spectra of 4⊂1 in H2O. (C) Decay of fluorescence of 4 and 4⊂1 at three different wavelengths.
For nanosecond-to-microsecond transient absorption measurements on 2 and \( 2 \subset 1 \), the same excitation beam as described on p. S40 was used in combination with an EOS–Sub-Nanosecond Transient Absorption Spectrometer (Ultrafast Systems, USA). The measurement was based on combining the ultrashort pump pulse with a white-light continuum generated by a photonic crystal fiber, thereby allowing for longer delays that are electronically triggered rather than using an optical delay line.

![Figure S65](image-url)

**Figure S65.** (A) Time-resolved absorption spectra of \( 2 \subset 1 \) in H\(_2\)O (replotted from Figure 2c in the main text). (B) Time-resolved absorption spectra of 2 in MeCN.

11. Competitive binding of BODIPY 2 vs azobenzene guests

We have previously demonstrated\(^1\) that azobenzene (Azo in Figure S66) and tetra-\(\alpha\)-fluoroazobenzene (F-Azo in Figure S66) can bind within the cavity of cage 1. Moreover, we roughly estimated the association constant of Azo, \( K_a = [Azo;\subset 1]/[1][Azo]^2 \), as \( \sim 10^9 \) M\(^{-2}\). Although determining the \( K_a \) of F-Azo was not possible, we hypothesized that the binding strength would be higher owing to the presence C–F····H hydrogen bond interactions.\(^1\) In order to obtain hints about the binding strength of the model BODIPY 2, we followed competitive binding of 2 vs Azo and 2 vs F-Azo in the presence of an equimolar amount of both guests with respect to cage 1 and in the presence of a three-fold excess of both guests with respect to 1. The blue trace in Figure S66A shows the UV–vis spectrum of an equilibrated mixture of cage 1, BODIPY 2, and Azo in a 1:1:1 molar ratio. When the amount of both guests was increased three times, absorbance at \( \sim 480 \) nm (due to encapsulated 2) increased slightly, whereas absorbance at 320 nm (due to encapsulated Azo) decreased (Figure S66A, red trace). This result indicates that in the presence of competition between 2 and Azo, BODIPY 2 is bound preferentially, i.e., its \( K_a \) is higher than \( 10^9 \) M\(^{-2}\). In contrast, when the amounts of 2 and F-Azo were increased from 1 equiv to 3 equiv with respect to the cage, we observed a drastic decrease in the amount of encapsulated 2 (blue and red spectra in Figure S66B, respectively), indicating that F-azo is bound significantly stronger than BODIPY 2.
Figure S66. (A) UV–vis absorption spectra of cage 1 equilibrated with 1 equiv of BODIPY 2 and 1 equiv of azobenzene (blue trace), and with 3 equiv of 2 and 3 equiv of azobenzene (red trace). (B) UV–vis absorption spectra of cage 1 equilibrated with 1 equiv of 2 and 1 equiv of tetra-o-fluoroazobenzene (blue trace), and with 3 equiv of 2 and 3 equiv of tetra-o-fluoroazobenzene (red trace).

12. Reversible switching between H- and J-aggregates of BODIPY 4

The addition of 4 in MeOH (20 µL) to an excess (980 µL) of water leads to the formation of J-type aggregates. These aggregates have a sharp absorbance band at >600 nm (the exact position, intensity, and shape of the band depend on the degree of aggregation) and a sharp emission band at ~630 nm (the very small Stokes shift is characteristic of J-aggregates). When this solution of J-aggregates of 4 (77 µM) was treated with an excess of cage 1 in water, the J-aggregates’ absorbance band rapidly decreased as a result of the encapsulation of 4 within 1 as an H-type dimer.

Figure S67 shows the changes in the UV–vis spectra of 4 during titration with aliquots of 1. The band due to J-aggregates can no longer be seen after the addition of 0.5 equiv of 1, whereas the H-dimer band increases until ~0.8 equiv of 1 has been added, in agreement with the ~60% encapsulation yield of 4 within 1. The J-to-H-aggregate transition can also be followed by fluorescence spectroscopy, which showed a decrease in the ~630 nm sharp emission band accompanied by a rapid increase in a broader, more intense band at ~585 nm (Figure S68). Remarkably, the addition of 1 equiv of the cage broke the J-aggregates of 4 and induced the formation of $4\subset 1$ within only ~30 s.

Figure S67. Titration of 4 aggregated in 1:49 MeOH:H$_2$O (77 µM) with 1 to yield $4\subset 1$. 
Figure S68. Changes in the fluorescence emission ($\lambda_{exc} = 530$ nm) of 4 aggregated in 1:49 MeOH:H$_2$O (39 $\mu$M) after adding 1 equiv of 1.

We hypothesized that the H-to-J-aggregate transition accompanying the encapsulation of 4 could be reversed by a controlled disassembly of cage 1, and that such disassembly could be achieved using aqueous KCN, which forms a strong complex with Pd$^{2+}$. To verify that KCN can decompose the cage, a solution of 10 mg (3.14 $\mu$mol) of 1 in 0.7 mL of D$_2$O in an NMR tube was treated with aliquots of 100 mM aqueous (D$_2$O) KCN. After the addition of each aliquot of KCN (which induced the precipitation of a white solid), the NMR tube was shaken and an NMR spectrum was recorded.

Cyanide CN$^-$ is a strong ligand for Pd$^{2+}$; therefore, the addition of KCN gradually displaces the TIm (1,3,5-trimidazoylbenzene, “trimidazole”) and TMEDA ($N,N,N',N'$-tetramethylethylenediamine) ligands from the Pd$^{2+}$ centers, resulting ultimately in the formation of the [Pd(CN)$_4$]$^{2-}$ complex. Interestingly, the addition of 1.0 equiv of KCN (with respect to the Pd$^{2+}$ centers) is sufficient to remove all the TIm ligands from the solution (TIm’s aromatic protons are no longer detectable; Figure S69). Further addition of KCN replaces the bidentate TMEDA ligands; the NMR spectrum after the addition of 4.0 equiv corresponds to that of free TMEDA in water (two singlets at 2.55 ppm and 2.26 ppm, corresponding to TMEDA’s CH$_2$ and CH$_3$ groups; Figure S69).
Figure S69. Changes in the $^1$H NMR spectra of 1 during the gradual addition of KCN (400 MHz, D$_2$O, 298 K) (the numbers of equivalents of KCN with respect to the Pd$^{2+}$ centers).

Having established that KCN can readily disassemble cage 1, we studied its effect on inclusion complex 4⊂1. When a solution of 4⊂1 in water was titrated with aqueous KCN, the formation of J-aggregates of 4 was observed by UV–vis spectroscopy (see Figure S70). Notably, a substoichiometric amount of KCN was sufficient to restore the full intensity of the J-aggregate band. This process could also be followed by fluorescence spectroscopy (see Figure S71).

Figure S70. Changes in the absorption spectrum of 4⊂1 in H$_2$O (75 μM) during titration with KCN (the number of equivalents with respect to Pd$^{2+}$). Note the non-monotonous change in the absorbance at $\lambda = 548$ nm (corresponding to the wavelength of the maximum absorption of free 4 in MeCN), which increases from ~0.73 (at t = 0) to ~0.83 (for 0.6 equiv KCN) and then decreases to ~0.79 (for 1.0 equiv KCN). This result strongly suggests the presence of free 4 as an intermediate between the H-aggregate 4⊂1 and the J-aggregate 4∞.
Figure S71. Changes in the fluorescence spectrum ($\lambda_{\text{exc}} = 530$ nm) of $4_2 \subset 1$ in H$_2$O (39 μM) following the injection of KCN (0.8 equiv with respect to Pd$^{2+}$) followed over time.

Finally, we hypothesized that the pronounced color change caused by treating $4_2 \subset 1$ with KCN could be used to detect the presence of cyanide in water. To demonstrate a proof-of-concept system for cyanide detection, we soaked small pieces of agarose gels with aqueous $4_2 \subset 1$ and treated them with KCN, among other inorganic salts (see Figure S72). We found that the only other salt causing visual changes similar to those induced by cyanide was thiocyanate, although it took significantly longer for color change to appear.

Figure S72. (A) Two pieces of agarose gel (10×10×1 mm; prepared using 1 g of agarose and 50 mL of H$_2$O) soaked with aqueous $4_2 \subset 1$ (2 mL; 0.5 μM). (B) Left: a 10×10×1 mm piece of agarose gel soaked with aqueous $4_2 \subset 1$ (2 mL; 0.5 μM) following immersion in a 760 μM KCN solution (2 mL) for 10 min. Right: a control sample not exposed to KCN. (C) A larger (60×50×1 mm) piece of agarose gel soaked with a 0.5 μM $4_2 \subset 1$ and exposed to different salts (150 nmol each): KCN (1), KCl (2), NaI (3), NaSCN (4), Na$_2$SO$_4$ (5), NaNO$_3$ (6), and AcOK (7). The photograph was taken 10 min after applying droplets of the salt solutions. For KCN, the color change was immediate; for NaSCN, it took several minutes. We have also tested HCl, Na$_2$SO$_3$, and NaOH (10 μL of 100 mM solutions, corresponding to 1 μmol); HCl and Na$_2$SO$_3$ did not cause any visual changes; NaOH induced the decomposition of BODIPY and rendered the gel colorless.
13. X-ray data collection and structure refinement

Single crystals of inclusion complexes 2\(_2\subset\)1, 3\(_3\subset\)1, and 4\(_4\subset\)1 were obtained by slow evaporation of water from their respective aqueous solutions. Single crystals of 3 were obtained by slow evaporation of CH\(_2\text{Cl}_2\) from a CH\(_2\text{Cl}_2\)/hexane solution mixture of 3. All crystals were coated in Paratone oil (Hampton Research) and mounted on MiTeGen loops. They were flash frozen in a liquid nitrogen stream of the Oxford Cryostream system. Data collection was performed under a stream of nitrogen at 100 K. The diffraction data of 2\(_2\subset\)1 and 4\(_4\subset\)1 were collected on a Rigaku XtaLAB\(^{\text{PRO}}\) diffractometer using Cu-K\(_\alpha\) radiation (1.54184 Å) and processed with CrysAlisPRO. The diffraction data of 3 and 3\(_3\subset\)1 were collected on a Bruker APEX-II Kappa CCD diffractometer using Mo-K\(_\alpha\) radiation (0.7107 Å) and processed with Bruker SAINT. The structures were solved by direct methods using SHELXT. All non-hydrogen atoms were further refined by SHELXL with anisotropic displacement coefficients. Hydrogen atoms were placed in calculated positions

| Species | 3 | 2\(_2\subset\)1 | 3\(_3\subset\)1 | 4\(_4\subset\)1 |
|---------|---|-------------|-------------|-------------|
| CCDC No. | 1990914 | 1551436 | 1990915 | 1990916 |
| Formula * | C\(_{16}\)H\(_{10}\)BF\(_3\)N\(_2\)O | C\(_{25}\)H\(_{17}\)BF\(_3\)F\(_4\)N\(_8\) | C\(_{25}\)H\(_{16}\)BF\(_3\)F\(_6\)N\(_{10}\) | C\(_{24}\)H\(_{12}\)BF\(_3\)F\(_4\)N\(_8\) |
| Formula weight | 304.14 | 3711.68 | 7518.46 | 4027.16 |
| Crystal system | Monoclinic | Monoclinic | Triclinic | Monoclinic |
| Space group | \(P2_1/c\) | \(P2_1\) | \(P1\) | \(P2_1/c\) |
| Crystal size (mm) | 0.20×0.20×0.20 | 0.29×0.28×0.10 | 0.23×0.13×0.04 | 0.06×0.04×0.03 |
| Crystal color and shape | Purple prism | Red prism | Red plate | Purple plate |
| Temperature (K) | 100 | 100 | 100 | 100 |
| Wavelength (Å) | 0.71073 | 1.54184 | 0.71073 | 1.54184 |
| \(a\) (Å) | 16.6385(9) | 15.0428(1) | 18.784(2) | 14.93362(6) |
| \(b\) (Å) | 12.1506(6) | 41.8036(2) | 20.018(2) | 42.0135(2) |
| \(c\) (Å) | 14.9855(8) | 15.4289(1) | 29.223(2) | 15.34383(7) |
| \(\alpha\) (°) | 90 | 90 | 72.80(1) | 90 |
| \(\beta\) (°) | 103.585(2) | 95.093(1) | 73.439(4) | 94.5872(4) |
| \(\gamma\) (°) | 90 | 90 | 65.09(4) | 90 |
| Volume (Å\(^3\)) | 2944.9(3) | 9664.1(1) | 7518.42 | 9596.09(7) |
| \(Z\) | 8 | 2 | 1 | 2 |
| \(\rho_{\text{calc}}\) (g cm\(^{-3}\)) | 1.372 | 1.276 | 1.334 | 1.394 |
| \(\mu\) (mm\(^{-1}\)) | 0.102 | 5.062 | 0.645 | 5.243 |
| No. of reflections (unique) | 25986(5389) | 39555(20061) | 121838(34262) | 146699(18217) |
| \(R_{\text{int}}\) | 0.0404 | 0.1016 | 0.097 | 0.0390 |
| Completeness to \(2\theta\) (%) | 99.8 | 99.0 | 99.3 | 99.8 |
| Data / restraints / parameters | 5378 / 0 / 416 | 39275 / 1056 / 2151 | 34031 / 289 / 2240 | 18187 / 111 / 1206 |
| Goodness-of-fit on \(F^2\) | 1.053 | 1.061 | 0.918 | 1.020 |
| Final \(R_1\) and \(wR_2\) indices \([I>2\sigma(I)]\) | 0.0601, 0.1531 | 0.0795, 0.2192 | 0.0718, 0.1809 | 0.0727, 0.2056 |
| \(R_1\) and \(wR_2\) indices (all data) | 0.0791, 0.1687 | 0.0829, 0.2253 | 0.1262, 0.2040 | 0.0747, 0.2080 |

Table S3. Crystallographic data. *Derived from the crystal structure.
14. Supplementary references

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