Electrical Supplementary Information

An Aqueous Molecular Tube with Polyaromatic Frameworks Capable of Binding Fluorescent Dyes

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Materials and methods


Scheme S1. Previous synthetic route of tube 1’.
Synthesis of 3-bromo-5-methoxyphenylboronic acid pinacol ester
KH-268, (283, 296)

1,3-Dibromo-5-methoxybenzene (2.010 g, 7.558 mmol) and dry THF (100 mL) were added to a 2-necked 200 mL glass flask filled with N₂. A hexane solution (2.69 M) of n-butyllithium (3.0 mL, 7.8 mmol) was then added dropwise to this flask at –80 ºC under N₂. After the mixture was stirred at –80 ºC for 1 h, a dry THF solution (5 mL) of B(OMe)₃ (1.0 mL, 9.0 mmol) was added to the solution. The resultant mixture was further stirred at –80 ºC for 1 h and then warmed to r.t. for 1 h. Pinacol (1.280 g, 1.083 mmol) and AcOH (1 mL) were added to the solution and the resultant solution was stirred at r.t. for 24 h. The products were extracted with CH₂Cl₂ and the combined organic phase was dried over MgSO₄, filtrated, and concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography (hexane:ethyl acetate = 10:1) to afford 3-bromo-5-methoxyphenylboronic acid pinacol ester as a yellow solution (1.975 g, 6.310 mmol, 83%).
Synthesis of anthracene dimer 3b

Anthracene dimer 3a (7.762 g, 15.82 mmol) and THF (100 mL) were added to a 200 mL glass flask. 1,3-Diiodo-5,5-dimethylhydantoin (DIH; 8.036 g, 20.43 mmol) was added to the solution at 0 °C and then concentrated H2SO4 (0.5 mL) was added to the solution. The resultant mixture was stirred at r.t. for 1 d. A precipitated crude product was washed with CH3OH, H2O, and hexane to afford 3b as a yellow solid (7.679 g, 10.34 mmol; 65%).

1H NMR (400 MHz, CDCl3, r.t.): δ 8.54 (d, J = 8.8 Hz, 4H), 7.86 (d, J = 8.8 Hz, 4H), 7.57-7.52 (m, 4H), 7.46-7.43 (m, 4H), 7.15 (s, 1H), 6.97 (s, 1H), 3.78 (s, 6H). 13C NMR (100 MHz, CDCl3, r.t.): δ 159.1 (Cq), 136.5 (CH), 135.5 (Cq), 134.0 (CH), 133.8 (Cq), 131.7 (Cq), 127.6 (CH), 127.5 (CH), 125.8 (CH), 119.2 (Cq), 105.9 (Cq), 96.3 (CH), 56.2 (CH3). FT-IR (KBr, cm−1): 3440, 3068, 2942, 2836, 1606, 1506, 1450, 1330, 1261, 1201, 1157, 1029, 866, 752. MALDI-TOF MS (dithranol): m/z Calcd. for C36H24I2O2 [M]+ 741.99, Found 741.80.
**Figure S1.** $^1$H NMR spectrum (400 MHz, CDCl$_3$, r.t.) of 3b.

**Figure S2.** $^{13}$C NMR spectrum (100 MHz, CDCl$_3$, r.t.) of 3b.
**Synthesis of half-tube 2a**

Anthracene dimer 3b (1.952 g, 2.629 mmol), 3-bromo-5-methoxyphenylboronic acid pinacol ester (1.975 g, 6.310 mmol), Pd(PPh₃)₄ (0.154 g, 0.133 mmol), and toluene (150 mL) were added to a 2-necked 100 mL glass flask filled with N₂. A degassed aqueous solution (25 mL) of Na₂CO₃ (3.824 g, 36.07 mmol) was added to this flask and the resultant mixture was stirred at 100 °C for 48 h. The mixture was concentrated under reduce pressure and the crude product was extracted with CHCl₃. The obtained crude product was purified by silica-gel column chromatography (hexane:ethyl acetate = 10:1) and GPC (CHCl₃) to afford half-tube 2a as a yellow solid (1.233 g, 1.432 mmol; 54%).

**1H NMR (400 MHz, CDCl₃, r.t.):** δ 7.97 (d, J = 8.8 Hz, 4H), 7.68 (d, J = 8.8 Hz, 4H), 7.43 (dd, J = 8.8, 7.6 Hz, 4H), 7.36 (dd, J = 8.8, 7.6 Hz, 4H), 7.29 (s, 1H), 7.26 (s, 1H, overlapped by CHCl₃), 7.24 (s, 2H), 7.16 (s, 1H), 7.03-7.02 (m, 2H), 6.89 (s, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.84 (s, 3H), 3.81 (s, 3H).

**13C NMR (100 MHz, CDCl₃, r.t.):** δ 160.4 (Cq), 159.1 (Cq), 142.4 (Cq), 137.1 (CH), 135.2 (Cq), 134.1 (Cq), 130.5 (Cq), 129.9 (Cq), 127.1 (CH), 126.9 (CH), 126.8 (CH), 125.4 (CH), 125.2 (CH), 123.0 (Cq), 119.5 (Cq), 116.7 (CH), 116.1 (CH), 96.3 (CH), 56.2 (CH₃), 55.8 (CH₃).

**FT-IR (KBr, cm⁻¹):** 3068, 3007, 2941, 2837, 1597, 1454, 1371, 1259, 1201, 1041, 847, 766.

**MALDI-TOF MS (dithranol):** m/z Calcd. for C₅₀H₃₆Br₂O₄+ [M]+ 860.10, Found 859.88. E.A.: Calcd. for C₅₀H₃₆Br₂O₄•0.5CH₂Cl₂: C, 67.16; H, 4.13. Found: C, 67.27; H, 4.00.
Figure S3. $^1$H NMR spectrum (400 MHz, CDCl$_3$, r.t.) of 2a.

Figure S4. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$, r.t.) of 2a.
Figure S5. $^1$H-$^1$H COSY spectrum (400 MHz, CDCl$_3$, r.t.) of 2a (aromatic region).

Figure S6. HSQC spectrum (400 MHz, CDCl$_3$, r.t.) of 2a (aromatic region).
**Synthesis of half-tube 2b**

KH-279, (286, 298)

Dry CH₂Cl₂ (50 mL) and half-tube 2a (0.500 g, 0.581 mmol) were added to a 2-necked 200 mL glass flask filled with N₂. A CH₂Cl₂ solution (1.0 M) of BBr₃ (5.4 mL, 5.4 mmol) was slowly added to the solution at 0 °C and then the combined solution was stirred at 40 °C for 12 h. The reaction was quenched with H₂O. The two layers were separated and the aqueous layer was extracted with CH₂Cl₂. The combined organic layers were dried over MgSO₄, filtrated, and concentrated under reduced pressure. The resultant solid was washed with H₂O and hexane to afford a yellow solid. The resulted solid, Cs₂CO₃ (1.21 g, 3.73 mmol), and dry CH₃CN (30 mL) were added to a 2-necked 300 mL glass flask filled with N₂. After the mixture was stirred at r.t. for 30 min,
chloromethyl methyl ether (0.45 g, 5.7 mmol) was added to the solution. The resultant solution was stirred at r.t. for 16 h. The reaction was quenched with H₂O. The crude product was extracted with CH₂Cl₂ and the combined organic phase was dried over MgSO₄, filtrated, and concentrated under reduce pressure. The crude product was purified by silica-gel column chromatography (hexane:ethyl acetate = 10:1) to give 2b as a yellow solid (0.400 g, 0.408 mmol, 70%).

¹H NMR (400 MHz, CDCl₃, r.t.): δ 8.00 (d, J = 8.4 Hz, 4H), 7.69 (d, J = 8.4 Hz, 4H), 7.47-7.35 (m, 12H), 7.29 (s, 1H), 7.22 (s, 1H), 7.15 (s, 1H), 7.02 (s, 1H), 5.24 (s, 2H), 5.19 (s, 2H), 5.11 (s, 4H), 3.53 (s, 3H), 3.49 (s, 3H), 3.49 (s, 3H), 3.22 (s, 3H), 3.20 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, r.t.): δ 158.2 (C₉), 156.6 (C₉), 148.4 (C₉), 137.0 (CH), 135.1 (C₉), 134.1 (C₉), 130.5 (C₉), 129.9 (C₉), 128.1 (CH), 127.2 (CH), 126.8 (CH), 125.9 (CH), 125.3 (CH), 122.9 (C₉), 122.2 (C₉), 118.9 (CH), 118.8 (CH), 118.5 (CH), 103.4 (CH), 95.0 (CH₃), 56.4 (CH₃). FT-IR (KBr, cm⁻¹): 3438, 3068, 2949, 2916, 2839, 1597, 1566, 1371, 1248, 1151, 1072, 1018, 920, 766. MALDI-TOF MS (dithranol): m/z Calcd. for C₅₄H₄₄Br₂O₈ [M]+ 980.14, Found 979.93. E.A.: Calcd. for C₅₄H₃₄Br₂O₈: C, 66.13; H, 4.52. Found: C, 66.13; H, 4.25.

![Figure S8](image)

Figure S8. ¹H NMR spectrum (400 MHz, CDCl₃, r.t.) of 2b.
Figure S9. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$, r.t.) of 2b.

Figure S10. MALDI-TOF MS spectrum (dithranol) of 2b.
Half-tube 2b (0.150 g, 0.153 mmol), Ni(cod)$_2$ (0.098 g, 0.36 mmol), 2,2'-bipyridyl (0.064 g, 0.41 mmol), and dry DMF (50 mL) were added to a 2-necked 100 mL glass flask filled with N$_2$ and the resultant mixture was stirred at 90 °C for 24 h. The reaction was quenched with H$_2$O. The two layers were separated and the aqueous layer was extracted with CH$_2$Cl$_2$. The combined organic layers were concentrated under reduced pressure and washed with H$_2$O, CH$_3$OH, and acetone. The crude product was purified by silica-gel column chromatography (hexane:CHCl$_3$ = 10:1) to give 1” as a yellow solid (0.037 g, 0.023 mmol, 30%).

$^1$H NMR (400 MHz, CDCl$_3$, r.t.): δ 7.82 (d, $J = 8.4$ Hz, 8H), 7.65 (m, 4H), 7.61 (d, $J = 8.4$ Hz, 4H), 7.40 (s, 2H), 7.27-7.18 (m, 24H), 7.03 (s, 2H), 5.34 (s, 8H), 5.04 (s, 8H), 3.60 (s, 12H), 3.19 (s, 12H). FT-IR (KBr, cm$^{-1}$): 3460, 3063, 2952, 2925, 2851, 2827, 1587, 1379, 1150, 1082, 1000, 923, 768. MALDI-TOF MS (dithranol): $m/z$ Calcd. for C$_{108}$H$_{88}$O$_{16}$ [M]$^+$ 1641.61, Found 1641.44. HR MS (ESI): $m/z$ Calcd. for C$_{108}$H$_{88}$O$_{16}$ [M]$^+$ 1641.6082, Found 1641.6082.
Figure S11. $^1$H NMR spectrum (400 MHz, CDCl$_3$, r.t.) of 1$''$.

Figure S12. MALDI-TOF MS spectrum (dithranol) of 1$''$. 
Synthesis of tube 1

Tube 1” (74.3 mg, 0.0452 mmol), THF (40 mL), and methanol (10 mL) were added to a 100 mL glass flask. Concentrated hydrochloric acid (50 mL) was added to this flask and stirred at 50 °C for 24 h. The mixture was concentrated under reduce pressure. The crude product was washed with H2O and CHCl3, and purified by silica-gel column chromatography (hexane:acetone = 1:1) to give a deprotected tube as a white solid. NaH (60% in oil; 44.5 mg, 1.11 mmol) was added to a 100 mL glass flask and washed with hexane under N2. The resultant deprotected tube and dry THF (20 mL) were added to this flask and stirred at r.t. for 1 h. 1,3-Propanesultone (0.135 g, 1.11 mmol) was added dropwise to this flask. The resultant mixture was stirred overnight at 80 °C. The mixture was concentrated under reduce pressure and the crude product was washed with ether, acetone, and 1-propanol to afford 1 as a yellow solid (54.9 mg, 0.0225 mmol, 50%).

1H NMR (400 MHz, CD3OD, r.t.): δ 7.79 (d, J = 8.4 Hz, 8H), 7.65 (s, 4H), 7.62 (d, J = 8.4 Hz, 4H), 7.31-7.22 (m, 18H), 7.12 (s, 4H), 7.09 (s, 4H), 6.83 (s, 2H), 4.33 (t, J = 6.0 Hz, 8H), 4.23 (t, J = 6.0 Hz, 8H), 3.12 (t, J = 7.6 Hz, 8H), 2.47 (t, J = 7.6 Hz, 8H), 2.37 (q, J = 7.2 Hz, 8H), 1.95 (q, J = 7.2 Hz, 8H). 13C NMR (100 MHz, CD3OD, r.t.): δ 161.2 (Cq), 159.4 (Cq), 142.7 (Cq), 142.5 (Cq), 137.9 (CH), 137.5 (Cq), 134.9 (Cq), 131.5 (Cq), 131.0 (Cq), 127.9 (CH), 127.8 (CH), 126.1 (CH), 125.9 (CH), 123.0 (CH), 121.1 (Cq), 118.1 (CH), 113.4 (CH), 99.9 (CH), 68.6 (CH2), 68.2 (CH2), 49.4-48.6 (overlapped with MeOH), 26.5 (CH3), 26.1 (CH3). FT-IR (KBr, cm⁻¹): 3451, 1504, 1440, 1380, 1311, 1190, 1101, 1046, 801, 770, 606, 528. ESI-TOF MS (CH3OH): m/z 383.8 [1 – 6Na+]6-, 465.2 [1 – 5Na+]5-, 587.2 [1 – 4Na+]4-, 791.0 [1 – 3Na+]3-.
Figure S13. $^1$H NMR spectrum (400 MHz, CD$_3$OD, r.t.) of 1.

Figure S14. $^{13}$C NMR spectrum (100 MHz, CD$_3$OD, r.t.) of 1.
Figure S15. HSQC spectrum (400 MHz, CD$_3$OD, r.t.) of 1 (aliphatic region).

Figure S16. HSQC spectrum (400 MHz, CD$_3$OD, r.t.) of 1 (aromatic region).
Figure S17. ESI-TOF MS spectrum (CH$_3$OH) of 1.

Figure S18. (a) UV-vis (10 µM, r.t.) and (b) fluorescence spectra ($\lambda_{ex} = 377$ nm, 10 µM, r.t.) of 1" in CH$_2$Cl$_2$ and 1 in H$_2$O and CH$_3$OH.
Synthesis and properties of 1⊃(4a)₂

Coumarin 337 (4a; 0.05 mg, 0.2 µmol) was added to an H₂O solution (0.5 mL) of tube 1 (0.25 mg, 0.10 µmol) in a glass test tube. The solution was stirred at r.t. for 1 h. After filtration, the quantitative formation of a 1⊃(4a)₂ complex was confirmed by UV-vis, fluorescence, DLS, and MS analyses.


Figure S19. ESI-TOF MS spectrum (H₂O) of 1⊃(4a)₂.
Figure S20. $^1$H NMR spectra (400 MHz, r.t.) of tube 1 in (a) CD$_3$OD, (b) D$_2$O and (c) D$_2$O (at 80 ºC), and (d) 1⊃(4a)$_2$ in D$_2$O.

Figure S21. Particle size distribution (H$_2$O, r.t.) of (a) 1 and (b) 1⊃(4a)$_2$ by DLS analysis.

Figure S22. (a) Titration UV-vis spectra (0.2 mM, H$_2$O, r.t.) and (b) the plot ($\lambda_{max} = 446$ nm) of 1 by the addition of 4a ([4a]/[1] = 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0).
Figure S23. (a) Titration fluorescence spectra ($\lambda_{ex} = 378$ nm, 0.2 mM, H$_2$O, r.t.) of 1 by the addition of 4a ([4a]/[1] = 0.5, 1.0, 1.5, 2.0), and (b) fluorescence spectra (0.2 mM, H$_2$O, r.t.) of 1[4a]$^2$ upon irradiation at $\lambda_{ex} = 378$, 446, and 480 nm, and (c) fluorescence spectra (0.2 mM, H$_2$O, r.t.) of 1 and 1[4a]$^2$ for the estimation of the FRET efficiency ($E_{FRET} = 1 - I/I_0$).

Figure S24. (a) UV-vis spectra (r.t.) and (b) fluorescence spectra ($\lambda_{ex} = 378$ nm r.t.) of 1[4a]$^2$ in H$_2$O (0.2 mM), 1 + 4a in CH$_3$OH (0.2 mM), and 4a in CH$_3$OH (0.4 mM).
**Figure S25.** Fluorescent lifetime ($\lambda_{ex} = 365$ nm, 10 µM, H$_2$O, r.t.) of (a) 1 ($\lambda_{em} = 440$ nm) and (b) 1$\supset$4a$_2$ ($\lambda_{em} = 600$ nm).

**Table S1.** Fluorescent lifetime of 1 and 1$\supset$4a$_2$.

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$^a$ $<\tau> = (A_1\tau_1 + A_2\tau_2 + A_3\tau_3)/(A_1 + A_2 + A_3)$

**Figure S26.** Optimized structure of a 1$\supset$4a$_2$ complex.
Coumarin 334 (4b; 0.06 mg, 0.2 µmol) was added to an H2O solution (0.5 mL) of tube 1 (0.25 mg, 0.10 µmol) in a glass test tube. The solution was stirred at r.t. for 1 h. After filtration, the quantitative formation of a 1⊃(4b)2 complex was confirmed by UV-vis, fluorescence, and ESI-TOF MS analyses.

ESI-TOF MS (H2O): m/z 406.9 [1⊃(4b)2 – 7Na+]7–, 478.4 [1⊃(4b)2 – 6Na+]6–, 578.7 [1⊃(4b)2 – 5Na+]5–, 792.1 [1⊃(4b)2 – 4Na+]4–, 979.8 [1⊃(4b)2 – 3Na+]3–.

**Figure S27.** ESI-TOF MS spectrum (H2O) of 1⊃(4b)2.
**Figure S28.** (a) Titration UV–vis spectra (0.2 mM, H₂O, r.t.) and (b) the plot ($\lambda_{\text{abs}} = 455$ nm) of 1 by the addition of 4b ([4b]/[1] = 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0).

**Figure S29.** (a) Titration fluorescence spectra ($\lambda_{\text{ex}} = 378$ nm, 0.2 mM, H₂O, r.t.) of 1 by the addition of 4b ([4b]/[1] = 0.5, 1.0, 1.5, 2.0), and (b) fluorescence spectra (0.2 mM, H₂O, r.t.) of 1 and $1\supset(4b)_2$ for the estimation of the FRET efficiency ($E_{\text{FRET}} = 1 - I/I_0$).

**Figure S30.** Optimized structure of a $1\supset(4b)_2$ complex.
Coumarin 153 (4c; 0.06 mg, 0.2 µmol) was added to an H₂O solution (0.5 mL) of tube 1 (0.25 mg, 0.10 µmol) in a glass test tube. The solution was stirred at r.t. for 1 h. After filtration, the formation of a 1⊂4c complex (40%) was confirmed by UV-vis, fluorescence, and ESI-TOF MS analyses. ESI-TOF MS (H₂O): m/z 320.9 [1⊂4c – 8Na⁺]⁸⁻, 370.1 [1⊂4c – 7Na⁺]⁷⁻, 435.6 [1⊂4c – 6Na⁺]⁶⁻, 527.3 [1⊂4c – 5Na⁺]⁵⁻, 664.6 [1⊂4c – 4Na⁺]⁴⁻.

Figure S31. ESI-TOF MS spectrum (H₂O) of 1⊂4c.
**Figure S32.** (a) Titration UV-vis spectra (0.2 mM, H₂O, r.t.) and (b) the plot (λ_{abs} = 437 nm) of 1 by the addition of 4c ([4c]/[1] = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0).

**Figure S33.** Titration fluorescence spectra (λ_{ex} = 378 nm, 0.2 mM, H₂O, r.t.) of 1 by the addition of 4c ([4c]/[1] = 0.1, 0.2, 0.3, 0.4, 0.5).

**Figure S34.** Optimized structure of 1–4c complex.
Synthesis and properties of host-guest complex 1⊃4d

Coumarin 334 (4d; 0.07 mg, 0.2 µmol) was added to an H₂O solution (0.5 mL) of tube 1 (0.25 mg, 0.10 µmol) in a glass test tube. The solution was stirred at r.t. for 1 h. After filtration, the formation of a 1⊃4d complex (30%) was confirmed by UV-vis, fluorescence, and ESI-TOF MS analyses.

ESI-TOF MS (H₂O): m/z 375.5 [1⊃4d – 7Na⁺]⁻, 441.9 [1⊃4d – 6Na⁺]⁻, 534.7 [1⊃4d – 5Na⁺]⁻, 674.3 [1⊃4d – 4Na⁺]⁻.

**Figure S35.** ESI-TOF MS spectrum (H₂O) of 1⊃4d.
**Figure S36.** (a) Titration UV-vis spectra (0.2 mM, H₂O, r.t.) and (b) the plot (λₘₐₓ = 430 nm) of 1 by the addition of 4d ([4d]/[1] = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0).

**Figure S37.** Titration fluorescence spectra (λₑₓ = 378 nm, 0.2 mM, H₂O, r.t.) of 1 by the addition of 4d ([4d]/[1] = 0.1, 0.2, 0.3, 0.4, 0.5).

**Figure S38.** Optimized structure of a 1⊂4d complex.
Figure S39. CIE chromaticity diagram ($\lambda_{ex} = 378$ nm, 0.2 mM, H$_2$O, r.t.) of 1, 4a-d, 1⊃(4a)$_2$, 1⊃(4b)$_2$, 1⊃4c, and 1⊃4d.

**Competitive binding experiment of coumarin guests**

![Diagram showing competitive binding experiment](image)

Coumarin dyes 4a and 4b (1.0 $\mu$mol each) were added to an H$_2$O solution (0.5 mL) of tube 1b (0.025 mg, 0.10 $\mu$mol) in a glass test tube. The solution was stirred at r.t. for 3 h. After filtration, the formation of host-guest complexes was confirmed by UV-vis analysis. Similarly, competitive binding experiments of coumarin guests, 4a vs. 4c, 4a vs. 4d, 4b vs. 4c, and 4b vs. 4d were examined.
Figure S40. Fluorescent spectra (λ<sub>ex</sub> = 378 nm, 0.2 mM, H<sub>2</sub>O, r.t.) of competitive binding experiments after mixing (a) 1+4a+4b, (b) 1+4a+4c, (c) 1+4a+4d, (d) 1+4b+4c, (e) 1+4b+4d, and (f) 1+4c+4d in H<sub>2</sub>O for 3 h at r.t.