Supporting Information

General Methods and Materials ................................................................. S2

Syntheses of Dehydrobenz[18]annulene (DBA) 1 ...................................... S3

Syntheses of Dehydrobenz[18]annulene (DBA) 2 ...................................... S4

NMR Spectra of DBAs 1 and 2 ............................................................... S5

Single Crystal Structures and Analyses .................................................... S7

Computational Analyses ........................................................................ S10

Solution-Phase Absorption and Emission Spectra of 1 and 2 .................. S11

References ............................................................................................. S12
General Methods and Materials

All reactions were performed under nitrogen in oven-dried glassware. Reagents bought from commercial suppliers were used without further purification. Reagents were purchased from following suppliers: 1,2-diiodotetrafluorobenzene (SynQuest), PdCl₂(PPh₃)₂ (Sigma), CuI (Sigma), dry PhMe (Sigma), NEt₃ (Oakwood), and 1,3-diiodobenzene (Oakwood). Dry PhMe was used after bubbling nitrogen through it for 3 h and NEt₃ was dried by distilling over KOH. Compounds 1,3-diethynylbenzene (4)¹ and methyl-3,5-diethynylbenzoate (5)² were synthesized using literature procedures.

Column chromatography was performed on silica gel 60, 32-63 mesh and analytical TLC on J. T. Baker plastic-backed silica gel IB-F plates. ¹H and ¹⁹F NMR spectra were collected on JEOL ECA-500 MHz or ECA-600 MHz spectrometers with working frequencies of 500 and 600 MHz, respectively, for ¹H nuclei. Chemical shifts are given in ppm (δ) with respect to the solvent peak or tetramethylsilane as a standard for ¹H NMR spectra and trifluorotoluene (PhCF₃, δ = −63.72 ppm) for ¹⁹F NMR spectra. Carbon NMR spectra are not included since the extensive coupling between ¹³C and ¹⁹F resulted in complex peaks with very low low intensities. NMR spectra were collected either at 25 or 40 °C.

Mass spectrometric analyses were performed by the Mass Spectrometry Facility of the Department of Chemistry and Biochemistry at the University of Texas at Austin. Melting points were recorded using a Barnstead International Mel-TEMP apparatus. Infrared spectra were recorded on a Nicolet iS10 FT-IR spectrometer equipped with a Thermo Scientific iTR for multi-purpose ATR sampling. Melting points were measured in open capillary tubes using a Barnstead International Mel-TEMP apparatus and are uncorrected. The solvent used for absorption and emission spectra measurements was chloroform of spectrophotometric grade. Absorption spectra were recorded using a PerkinElmer LAMBDA 25 UV/Vis spectrometer, and the emission spectra were measured on a PerkinElmer LS 55 fluorimeter.

Experiments are presented in the order following the discussion of the manuscript.

Compound numbers are identical to those in the main text of the manuscript.
A one-liter two-neck round bottom flask was equipped with a stir bar and charged with PdCl$_2$(PPh$_3$)$_2$ (0.175 g, 0.25 mmol) and CuI (0.048 g, 0.25 mmol). One neck of the flask was sealed with a septum and the other neck was connected to the condenser. The flask was then evacuated and backfilled with nitrogen three times and left under nitrogen. Dry NEt$_3$ (500 mL) and dry PhMe (550 mL) were transferred via cannula into the round bottom flask and the reaction mixture was stirred at 80 °C. A homogenous solution of 1,2-diiodotetrafluorobenzene (3, 2.01 g, 5 mmol) and 1,3-diethynylbenzene (4, 0.69 mL, 5.25 mmol) was made in dry PhMe (20 mL). This solution was slowly added to the flask via a syringe pump at the rate of 2 mL h$^{-1}$, and the reaction was stirred at 80 °C for additional 3 days. After that, the hot solution was filtered to remove the salts and catalyst. The filtrate was washed with water, saturated aqueous solution of NH$_4$Cl, and brine, and dried over MgSO$_4$. Then it was passed through a Celite pad and washed with PhMe. The solvent was removed using rotary evaporator to give a viscous crude product. Acetone was added to that crude material and the suspension was filtered off to remove most side products. The filtrate was then evaporated and the obtained solid was recrystallized in PhMe/Me$_2$CO, followed by PhMe/MeCN mixture to get the pure macrocycle 1 in 22% yield (297 mg, 0.54 mmol) as a light brown solid. mp 305–310°C (decomp). $^1$H NMR (600 MHz, C$_6$D$_6$, 40 °C) δ 7.95 (s, 2H), 7.20 (d, $J = 7.6$ Hz, 4H), 6.71 (t, $J = 7.6$ Hz, 2H) ppm. $^{19}$F NMR (565 MHz, C$_6$D$_6$, 40 °C) δ −134.46 (d, $J = 17.3$ Hz, 4F), −153.05 (d, $J = 17.3$ Hz, 4F) ppm. HRMS (Cl, [M]$^-$) $m/z$ Calcd. for C$_{32}$H$_8$F$_8$: 544.0498, found 544.0504. FT-IR (neat) $\tilde{\nu}$ 2215, 1624, 1502, 1485, 1120, 995, 966 cm$^{-1}$. 

Syntheses of Dehydrobenz[18]annulene (DBA) 1
Synthesis of Dehydrobenz[18]annulene (DBA) 2

A one-liter two-neck round bottom flask equipped with a stir bar was charged with PdCl₂(PPh₃)₂ (0.175 g, 0.25 mmol) and CuI (0.048 g, 0.25 mmol). One neck of the flask was sealed with a septum and the other neck was connected to the condenser. The flask was then evacuated and backfilled with nitrogen three times and left under nitrogen. Dry NEt₃ (200 mL) and dry PhMe (550 mL) were then added via a cannula into the round bottom flask and the reaction mixture was stirred at 80 °C. A homogenous solution of 1,2-diiodo-3,4,5,6-tetrafluorobenzene (3, 2.01 g, 5 mmol) and methyl 1,3-diethynylbenzoate (5, 0.97 g, 5.25 mmol) was made in dry PhMe (20 mL). Then the solution was slowly added to the flask via a syringe pump at the rate of 2 mL h⁻¹, and the reaction was stirred at 80 °C for 3 additional days. After that, the hot solution was filtered to remove the salts and catalyst. The filtrate then was washed with water, saturated aqueous solution of NH₄Cl, brine, and dried over MgSO₄. The solvent was removed using a rotatory evaporator. Acetone was added to the crude mixture and the suspension filtered off to remove most side products. Column chromatography of residue in DCM/hexane (1:1) gave a pure macrocycle 2. Some was also recovered from column chromatography of filtrate in DCM/hexanes (1:9). Together, macrocycle 2 was isolated in a 5% yield (79 mg, 0.12 mmol, Rf: 0.35) as a white solid. mp 308–311°C (decomposed). ¹H NMR (600 MHz, CDCl₃, 40 °C) δ 8.29 (s, 4H), 8.10 (s, 2H), 3.99 (s, 6H) ppm. ¹⁹F NMR (565 MHz, CDCl₃, 40 °C) δ −133.24 (d, J = 17.3 Hz, 1F), −152.02 (d, J = 13.0 Hz, 1F) ppm. HRMS (CI, [M⁻]) m/z Calcd for C₃₆H₁₂F₈O₄: 660.0608, found 660.0624. FT-IR (neat) ν 2219, 1729, 1624, 1504, 1486, 1437, 1240, 1128, 1023, 1003 cm⁻¹.
NMR Spectra of DBA 1 and 2

Figure S1. $^1$H NMR spectrum of DBA 1.

Figure S2. $^{19}$F NMR spectrum of DBA 1.
Figure S3. $^1$H NMR spectrum of DBA 2.

Figure S4. $^{19}$F NMR spectrum of DBA 2.
Single Crystal Structures and Analyses

All measurements were performed on a Bruker DUO platform diffractometer equipped with a 4K CCD APEX II detector and an Incoatec 30-Watt Cu microsource with compact multilayer optics. Data were collected using a narrow-frame algorithm with scan widths of 0.5% in omega and an exposure time of 20 s/frame at 4 cm detector distance. The data were integrated using the Bruker SAINT program, with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variations in the path length through the detector faceplate. The data were scaled, and an absorption correction was applied using SADABS. The structure was solved with SHELXT 2014 and refined with SHELXL 2018 using full-matrix least-squares refinement. The non-H atoms were refined with anisotropic thermal parameters, and all the H atoms were calculated in idealized positions and refined riding on their parent atoms.

Figure S5. Single crystal structure of DBA 1. Thermal ellipsoids are shown at 50% probability levels.

Table S1. Crystal data and structure refinement parameters for DBA 1.

| Identification code       | XW306   |
|---------------------------|---------|
| Empirical formula         | C_{32}H_{8}F_{8} |
| Formula weight            | 544.38  |
| Temperature / K           | 123(2)  |
| Crystal system            | Monoclinic |
| Space group               | P_{2_1}/n |
| a / Å                     | 10.5697(7) |
| b / Å                     | 5.0284(4)  |
| c / Å                     | 21.5838(14) |
| Parameter                      | Value                                      |
|-------------------------------|--------------------------------------------|
| $a / ^\circ$                  | 90                                         |
| $\beta / ^\circ$              | 100.063(5)                                 |
| $\gamma / ^\circ$             | 90                                         |
| Volume / Å$^3$                 | 1129.50(14)                                |
| $Z$                           | 2                                          |
| $\rho_{calc} / g/cm^3$        | 1.601                                      |
| Absorption coefficient / μmm$^{-1}$ | 1.216                                    |
| $F(000)$                      | 544.0                                      |
| Crystal size / mm$^3$         | $0.11 \times 0.02 \times 0.01$            |
| Radiation                     | CuK$\alpha$ ($\lambda = 1.5417$)          |
| Theta range for data collection | 8.32 to 132.02$^\circ$                    |
| Index ranges                  | $-12 \leq h \leq 12, -5 \leq k \leq 5, -25 \leq l \leq 24$ |
| Reflections collected         | 6508                                       |
| Independent reflections       | 1922 [$R_{int}=0.0343, R_{wp}=0.0314$]     |
| Data / restraints / parameters | 1922 / 0 / 181                             |
| Goodness-of-fit on $F^2$      | 1.033                                      |
| Final $R$ indexes [$I>2\sigma(I)$] | $R_I=0.0431, wR_I=0.1142$                 |
| $R$ indexes (all data)        | $R_I=0.0633, wR_I=0.1268$                  |
| Largest diff. peak / hole / e Å$^{-3}$ | 0.22 / −0.21                          |

**Figure S6.** Single crystal Structure of DBA 2. Thermal ellipsoids are shown at 50% probability levels.
Table S2. Crystal data and structure refinement parameters for DBA 2.

| Identification code          | 2-38-1_XW311            |
|-----------------------------|-------------------------|
| Empirical formula           | C_{36}H_{12}O_{4}F_{8}   |
| Formula weight              | 660.46                  |
| Temperature / K             | 123(2)                  |
| Crystal system              | Monoclinic              |
| Space group                 | P2_1/c                  |
| a / Å                       | 4.2883(2)               |
| b / Å                       | 23.3071(11)             |
| c / Å                       | 13.4627(6)              |
| α / °                       | 90                      |
| β / °                       | 94.375(3)               |
| γ / °                       | 90                      |
| Volume / Å³                 | 1341.65(11)             |
| Z                           | 2                       |
| ρ_{calc} g/cm³              | 1.635                   |
| Absorption coefficient (μ)/mm⁻¹ | 1.259                 |
| F(000)                      | 664.0                   |
| Crystal size / mm³          | 0.22 × 0.01 × 0.01      |
| Radiation                   | CuKα (λ = 1.5417)       |
| Theta range for data collection | 7.586 to 132.124°       |
| Index ranges                | −4 ≤ h ≤ 5, −27 ≤ k ≤ 24, −15 ≤ l ≤ 13 |
| Reflections collected       | 8753                    |
| Independent reflections     | 2303 [R_{int}=0.0336, R_{epr}=0.0325] |
| Data / restraints / parameters | 2303 / 0 / 218         |
| Goodness-of-fit on R^2      | 1.035                   |
| Final R indexes [R>2σ(b)]   | R_l=0.0385, wR_l=0.1076 |
| R indexes (all data)        | R_l=0.0482, wR_l=0.1139 |
| Largest diff. peak / hole / e Å⁻³ | 0.19 / −0.22         |
Computational Analyses

The calculations were carried out at the TD-B3LYP-D3/6-311+G(d,p) level of theory using the Gaussian16 software.\textsuperscript{3}

Figure S7. Computed HOMO–LUMO gap for DBA 1.

Figure S8. Computed HOMO–LUMO gap for DBA 2.
Optimized Cartesian coordinates

The geometries were optimized at the B3LYP-D3/6-31+G(d) level and the energies were further computed at the B3LYP-D3/6-311+G(d,p) level and include the ZPE correction.

**DBA 1 (C), \( N_{im} = 0 \), Electronic Energy + ZPE (Hartree) = -2022.981637**

| Atom | X    | Y    | Z    |
|------|------|------|------|
| F    | -3.6028 | 0.6494 | 0.0000 |
| F    | -3.6028 | -2.0787 | 0.0000 |
| F    | -1.2666 | -3.4423 | 0.0000 |
| F    | -1.2666 | 2.0130  | 0.0000 |
| C    | -2.4414 | -0.0171 | 0.0000 |
| C    | -2.4414 | -1.4122 | 0.0000 |
| C    | -1.2326 | -2.0995 | 0.0000 |
| C    | 0.0000  | -1.4293 | 0.0000 |
| C    | 1.2061  | -2.1702 | 0.0000 |
| C    | 2.2400  | -2.8097 | 0.0000 |
| C    | 3.4654  | -3.5353 | 0.0000 |
| C    | 4.6865  | -2.8410 | 0.0000 |
| H    | 4.6865  | -1.7579 | 0.0000 |
| C    | 5.9077  | -3.5354 | 0.0000 |
| C    | 7.1330  | -2.8097 | 0.0000 |
| C    | 8.1669  | -2.1702 | 0.0000 |
| C    | 0.0000  | 0.0000  | 0.0000 |
| C    | -1.2326 | 0.6702  | 0.0000 |
| C    | 5.8990  | -4.9459 | 0.0000 |
| H    | 6.8418  | -5.4843 | 0.0000 |
| C    | 4.6865  | -5.6356 | 0.0000 |
| H    | 4.6865  | -6.7220 | 0.0000 |
| C    | 3.4740  | -4.9459 | 0.0000 |
| H    | 2.5312  | -5.4843 | 0.0000 |
| F    | 12.9758 | -2.0786 | 0.0000 |
| F    | 12.9758 | 0.6494  | 0.0000 |
| F    | 10.6396 | 2.0130  | 0.0000 |
| F    | 10.6396 | -3.4423 | 0.0000 |
| C    | 11.8144 | -1.4122 | 0.0000 |
| C    | 11.8144 | -0.0171 | 0.0000 |
| C    | 10.6056 | 0.6702  | 0.0000 |
| C    | 9.3730  | 0.0000  | 0.0000 |
| C    | 8.1669  | 0.7408  | 0.0000 |
| C    | 7.1330  | 1.3804  | 0.0000 |
| C    | 5.9076  | 2.1060  | 0.0000 |
| C    | 4.6865  | 1.4117  | 0.0000 |
| H    | 4.6865  | 0.3285  | 0.0000 |
| C    | 3.4653  | 2.1060  | 0.0000 |
| C    | 2.2400  | 1.3804  | 0.0000 |
| C    | 1.2061  | 0.7408  | 0.0000 |
| C    | 9.3730  | -1.4293 | 0.0000 |
| C    | 10.6056 | -2.0995 | 0.0000 |
| C    | 3.4740  | 3.5166  | 0.0000 |
| H    | 2.5312  | 4.0550  | 0.0000 |
| C    | 4.6865  | 4.2062  | 0.0000 |
| H    | 4.6865  | 5.2926  | 0.0000 |
| C    | 5.8990  | 3.5166  | 0.0000 |
| H    | 6.8418  | 4.0549  | 0.0000 |
**DBA 1 \( (C) \), \( N_{\text{int}} = 0 \), Electronic Energy + ZPE (Hartree) = -2478.799904**

| Atom | X    | Y    | Z    |
|------|------|------|------|
| F    | -3.6070 | -2.0688 | 0.0000 |
| F    | -3.6001 | 0.6584  | 0.0000 |
| F    | -1.2606 | 2.0163  | 0.0000 |
| F    | -1.2743 | -3.4384 | 0.0000 |
| O    | 3.5106  | 6.2648  | 0.0000 |
| O    | 5.7690  | 6.3481  | 0.0000 |
| C    | 3.4803  | 7.7066  | 0.0000 |
| H    | 3.9798  | 8.0947  | 0.8919 |
| H    | 3.9798  | 8.0947  | -0.8919 |
| H    | 2.4228  | 7.9713  | 0.0000 |
| C    | 4.7373  | 5.7041  | 0.0000 |
| C    | 4.6828  | 4.2088  | 0.0000 |
| C    | 3.4703  | -4.9459 | 0.0000 |
| H    | 2.5405  | -5.5044 | 0.0000 |
| C    | 3.4593  | -3.5394 | 0.0000 |
| C    | 2.2324  | -2.8157 | 0.0000 |
| C    | 1.2013  | -2.1723 | 0.0000 |
| C    | -0.0035 | -1.4290 | 0.0000 |
| C    | 0.0000  | 0.0000  | 0.0000 |
| C    | 1.2081  | 0.7383  | 0.0000 |
| C    | 2.2413  | 1.3782  | 0.0000 |
| C    | 3.4664  | 2.1048  | 0.0000 |
| C    | 3.4692  | 3.5129  | 0.0000 |
| H    | 2.5302  | 4.0535  | 0.0000 |
| C    | -1.2373 | -2.0970 | 0.0000 |
| C    | -2.4444 | -1.4059 | 0.0000 |
| C    | -2.4409 | -0.0108 | 0.0000 |
| C    | -1.2304 | 0.6738  | 0.0000 |
| C    | 4.6891  | 1.4137  | 0.0000 |
| H    | 4.6915  | 0.3306  | 0.0000 |
| F    | 12.9759 | 0.6398  | 0.0000 |
| F    | 12.9690 | -2.0875 | 0.0000 |
| F    | 10.6296 | -3.4454 | 0.0000 |
| F    | 10.6433 | 2.0093  | 0.0000 |
| O    | 5.8584  | -7.6938 | 0.0000 |
| O    | 3.5999  | -7.7771 | 0.0000 |
| C    | 5.8886  | -9.1356 | 0.0000 |
| H    | 5.3891  | -9.5238 | -0.8919 |
| H    | 5.3891  | -9.5238 | 0.8919 |
| H    | 6.9461  | -9.4003 | 0.0000 |
| C    | 4.6316  | -7.1332 | 0.0000 |
| C    | 4.6861  | -5.6378 | 0.0000 |
| C    | 5.8987  | 3.5169  | 0.0000 |
| H    | 6.8285  | 4.0754  | 0.0000 |
| C    | 5.9097  | 2.1104  | 0.0000 |
| C    | 7.1365  | 1.3866  | 0.0000 |
| C    | 8.1676  | 0.7433  | 0.0000 |
| C    | 9.3725  | 0.0000  | 0.0000 |
| C    | 9.3689  | -1.4290 | 0.0000 |
| C    | 8.1609  | -2.1673 | 0.0000 |
| C    | 7.1277  | -2.8072 | 0.0000 |
| C    | 5.9025  | -3.5338 | 0.0000 |
| C    | 5.8998  | -4.9420 | 0.0000 |
| H    | 6.8388  | -5.4825 | 0.0000 |
| C    | 10.6062 | 0.6679  | 0.0000 |
| C    | 11.8134 | -0.0231 | 0.0000 |
| C    | 11.8098 | -1.4182 | 0.0000 |
### DBA 1 dimer, $N_{eq} = 0$, Electronic Energy + ZPE (Hartree) = -4046.013251

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| F    | 0.7760 | 0.4376 | -3.0967 |
| F    | 0.8128 | -2.2858 | -3.1183 |
| F    | 3.1130 | -3.6254 | -2.6331 |
| F    | 3.0381 | 1.8291 | -2.5739 |
| C    | 1.9234 | -0.2143 | -2.8622 |
| C    | 1.9432 | -1.6076 | -2.8784 |
| C    | 3.1310 | -2.2828 | -2.6227 |
| C    | 4.3233 | -1.5988 | -2.3478 |
| C    | 5.5134 | -2.3197 | -2.0916 |
| C    | 6.5369 | -2.9311 | -1.8564 |
| C    | 7.3900 | -3.6283 | -1.5509 |
| C    | 8.9034 | -2.9087 | -1.2381 |
| H    | 8.8781 | -1.8261 | -1.5509 |
| C    | 10.0947 | -3.5775 | -0.9145 |
| C    | 11.2658 | -2.8304 | -0.6037 |
| C    | 12.2586 | -2.1814 | -0.3381 |
| C    | 4.3018 | -0.1694 | -2.3271 |
| C    | 3.0911 | 0.4880 | -2.5872 |
| C    | 10.1127 | -4.9877 | -0.8981 |
| H    | 11.0318 | -5.5050 | -0.6409 |
| C    | 8.9566 | -5.7027 | -1.2109 |
| H    | 8.9774 | -6.7890 | -1.1997 |
| C    | 7.7747 | -5.0378 | -1.5372 |
| H    | 6.8729 | -5.5933 | -1.7745 |
| F    | 16.8480 | -2.0323 | 1.0900 |
| F    | 16.8121 | 0.6941 | 1.0922 |
| F    | 14.5651 | 2.0291 | 0.3894 |
| F    | 14.6375 | -3.4257 | 0.3879 |
| C    | 15.7327 | -1.3811 | 0.7377 |
| C    | 15.7143 | 0.0142 | 0.7389 |
| C    | 14.5540 | 0.6871 | 0.3736 |
| C    | 13.3897 | 0.0000 | 0.0000 |
| C    | 12.2201 | 0.7213 | -0.3368 |
| C    | 11.2032 | 1.3364 | -0.5916 |
| C    | 9.9903 | 2.0321 | -0.8564 |
| C    | 8.8441 | 1.3152 | -1.2341 |
| H    | 8.8942 | 0.2378 | -1.3334 |
| C    | 7.6281 | 1.9777 | -1.4638 |
| C    | 6.4642 | 1.2301 | -1.7963 |
| C    | 5.4677 | 0.5818 | -2.0477 |
| C    | 13.4080 | -1.4284 | 0.0000 |
| C    | 14.5908 | -2.0843 | 0.3712 |
| C    | 7.5691 | 3.3794 | -1.3260 |
| H    | 6.6266 | 3.8899 | -1.4957 |
| C    | 8.7094 | 4.0924 | -0.9560 |
| H    | 8.6564 | 5.1722 | -0.8471 |
| C    | 9.9144 | 3.4335 | -0.7157 |
| H    | 10.7984 | 3.9863 | -0.4134 |
| F    | -3.4403 | 0.6027 | -1.0898 |
| F    | -3.4039 | -2.1236 | -1.0903 |
| F    | -1.1566 | -3.4579 | -0.3873 |
| F    | -1.2298 | 1.9968 | -0.3889 |
DBA 2 dimer, $N_{im} = 0$, Electronic Energy + ZPE (Hartree) = −4957.662906

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| F    | 12.6507 | -0.9452 | -3.3254 |
| F    | 12.6432 | -3.6741 | -3.3370 |
| F    | 10.3024 | -5.0295 | -3.3509 |
| F    | 10.3216 | 0.4241  | -3.3289 |
| O    | 5.5009  | -9.2849 | -3.4782 |
| O    | 3.2672  | -9.3334 | -3.8187 |
| C    | 5.5181  | -10.7222| -3.5919 |
| H    | 4.8736  | -11.1709| -2.8307 |
| H    | 6.5591  | -11.0103| -3.4424 |
| H    | 5.1686  | -11.0272| -4.5821 |
| C    | 4.2882  | -8.7038 | -3.6300 |

S14
| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| C    | 4.3545    | -7.2129   | -3.5496   |
| C    | 5.5699    | 1.9338    | -3.2541   |
| H    | 6.4951    | 2.4991    | -3.2271   |
| C    | 5.5922    | 0.5273    | -3.2747   |
| C    | 6.8210    | -0.1905   | -3.2955   |
| C    | 7.8467    | -0.8404   | -3.3269   |
| C    | 9.0489    | -1.5848   | -3.3524   |
| C    | 9.0440    | -3.0133   | -3.3602   |
| C    | 7.8360    | -3.7566   | -3.3820   |
| C    | 6.8054    | -4.3936   | -3.4214   |
| C    | 5.5788    | -5.1154   | -3.4646   |
| C    | 5.5704    | -6.5238   | -3.5063   |
| H    | 6.5074    | -7.0680   | -3.5064   |
| C    | 10.2826   | -0.9184   | -3.3515   |
| C    | 11.4888   | -1.6098   | -3.3498   |
| C    | 11.4855   | -3.0050   | -3.3493   |
| C    | 10.2738   | -3.6880   | -3.3536   |
| C    | 4.3599    | -4.4199   | -3.4556   |
| H    | 4.3613    | -3.3380   | -3.4126   |
| F    | -3.9315   | -3.6411   | -3.2494   |
| F    | -3.9131   | -0.9128   | -3.2569   |
| F    | -1.5719   | 0.4354    | -3.3183   |
| F    | -1.6043   | -5.0188   | -3.3113   |
| O    | 3.1495    | 4.6476    | -3.3600   |
| O    | 5.3907    | 4.7685    | -3.0928   |
| C    | 3.0895    | 6.0880    | -3.3509   |
| H    | 3.7104    | 6.4970    | -4.1525   |
| H    | 2.0386    | 6.3315    | -3.5093   |
| H    | 3.4336    | 6.4683    | -2.3873   |
| C    | 4.3780    | 4.1083    | -3.2270   |
| C    | 4.3482    | 2.6141    | -3.2638   |
| C    | 3.1420    | -6.5166   | -3.5340   |
| H    | 2.2106    | -7.0714   | -3.5531   |
| C    | 3.1373    | -5.1124   | -3.4815   |
| C    | 1.9111    | -4.3908   | -3.4419   |
| C    | 0.8754    | -3.7575   | -3.3985   |
| C    | -0.3285   | -3.0153   | -3.3597   |
| C    | -0.3202   | -1.5869   | -3.3596   |
| C    | 0.8907    | -0.8564   | -3.3588   |
| C    | 1.9285    | -0.2266   | -3.3282   |
| C    | 3.1502    | 0.5012    | -3.3001   |
| C    | 3.1420    | 1.9079    | -3.2931   |
| H    | 2.1980    | 2.4390    | -3.2974   |
| C    | -1.5635   | -3.6794   | -3.3207   |
| C    | -2.7683   | -2.9839   | -3.2910   |
| C    | -2.7590   | -1.5886   | -3.3009   |
| C    | -1.5467   | -0.9087   | -3.3351   |
| C    | 4.3777    | -0.1801   | -3.2857   |
| H    | 4.3896    | -1.2634   | -3.2917   |
| F    | 12.9758   | 0.6254    | -0.1096   |
| F    | 12.9570   | -2.1029   | -0.1020   |
| F    | 10.6157   | -3.4508   | -0.0410   |
| F    | 10.6487   | 2.0034    | -0.0482   |
| O    | 5.8930    | -7.6622   | -0.0014   |
| O    | 3.6515    | -7.7824   | -0.2667   |
| C    | 5.9525    | -9.1026   | -0.0102   |
| H    | 5.3335    | -9.5110   | 0.7932    |
| H    | 7.0036    | -9.3464   | 0.1458    |
| H    | 5.6058    | -9.4834   | -0.9726   |
|  |  |  |  |
|---|---|---|---|
| C | 4.6645 | -7.1225 | -0.1333 |
| C | 4.6948 | -5.6283 | -0.0964 |
| C | 5.9028 | 3.5019 | 0.1734 |
| H | 6.8345 | 4.0564 | 0.1924 |
| C | 7.1332 | 1.3758 | 0.0816 |
| C | 8.1688 | 0.7423 | 0.0384 |
| C | 9.3726 | 0.0000 | 0.0000 |
| C | 9.3642 | -1.4284 | 0.0000 |
| C | 8.1533 | -2.1587 | -0.0010 |
| C | 7.1153 | -2.7883 | -0.0317 |
| C | 5.8934 | -3.5158 | -0.0598 |
| C | 5.9012 | -4.9224 | -0.0671 |
| H | 6.8451 | -5.4538 | -0.0631 |
| C | 10.6077 | 0.6639 | -0.0388 |
| C | 11.8124 | -0.0317 | -0.0682 |
| C | 11.8030 | -1.4270 | -0.0583 |
| C | 10.5906 | -2.1067 | -0.0243 |
| C | 4.6660 | -2.8341 | -0.0741 |
| H | 4.6545 | -1.7508 | -0.0678 |
| F | -3.6069 | -2.0678 | -0.0337 |
| F | -3.5991 | 0.6611 | -0.0232 |
| F | -1.2581 | 2.0163 | -0.0100 |
| F | -1.2779 | -3.4374 | -0.0297 |
| O | 3.5448 | 6.2710 | 0.1174 |
| O | 5.7788 | 6.3187 | 0.4569 |
| C | 3.5283 | 7.7084 | 0.2303 |
| H | 4.1729 | 8.1563 | -0.5314 |
| H | 2.4875 | 7.9969 | 0.0809 |
| H | 3.8782 | 8.0138 | 1.2201 |
| C | 4.7574 | 5.6894 | 0.2689 |
| C | 4.6906 | 4.1985 | 0.1888 |
| C | 3.4733 | -4.9477 | -0.1058 |
| H | 2.5479 | -5.5127 | -0.1327 |
| C | 3.4513 | -3.5412 | -0.0850 |
| C | 2.2227 | -2.8230 | -0.0639 |
| C | 1.1971 | -2.1731 | -0.0324 |
| C | -0.0050 | -1.4285 | -0.0072 |
| C | 0.0000 | 0.0000 | 0.0000 |
| C | 1.2082 | 0.7372 | 0.0214 |
| C | 2.2388 | 1.3799 | 0.0606 |
| C | 3.4657 | 2.1014 | 0.1040 |
| C | 3.4745 | 3.5098 | 0.1455 |
| H | 2.5376 | 4.0542 | 0.1456 |
| C | -1.2388 | -2.0948 | -0.0077 |
| C | -2.4449 | -1.4033 | -0.0096 |
| C | -2.4414 | -0.0081 | -0.0107 |
| C | -1.2297 | 0.6748 | -0.0068 |
| C | 4.6844 | 1.4056 | 0.0951 |
| H | 4.6827 | 0.3236 | 0.0523 |
Absorption and Emission Spectra in Solution of DBAs 1 and 2

With limited solubility of these macrocycles in hexanes and pentanes, the UV-vis absorption and fluorescence were investigated in chloroform. The absorption spectra in Figure S9A show the absorption band range for both DBAs between 250 and 375 nm, with $\lambda_{\text{max}}$ of 277 nm for DBA 1 and 275 nm for DBA 2. When excited at 342 nm at 1% transmission (Figure S9B), both macrocycles showed the similar peaks with the $\lambda_{\text{em}}$ for the DBA 1 at 381 nm and at 382 nm for DBA 2.

![Figure S9](image)

**Figure S9.** (A) The absorption spectra of DBA 1 (blue) at the concentration of 4.8 µM and DBA 2 (red) at the concentration of 3.7 µM (B). The emission spectra at $\lambda_{\text{ex}} = 342$ nm at 1% transmission of DBA 1 (blue) at 2.8 µM and macrocycle 2 (red) at 2.3 µM.
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