1. Synthetic details

All commercially available reagents were used as received, unless otherwise noted. Reagent grade solvents were distilled prior to use. Toluene and methanol were dried according to the standard procedures. Transformations with moisture-sensitive compounds were conducted under stream of argon. The reaction progress was monitored by thin-layer chromatography (TLC, silica gel 60 F_{254}). Product purifications were done by means of dry column vacuum
chromatography (DCVC) using silica gel Type D 5F.

The identity and purity of all synthesized compounds were confirmed by NMR techniques (measured on Varian 500MHz spectrometer with TMS as the internal reference), as well as by mass spectrometry via HRMS(ESI). All chemical shifts (δ) are given in ppm, coupling constants (J) are given in Hz. Dipyrrromethane 2 and corrole 3 were prepared according to the literature procedures.\textsuperscript{2,3}

10-[(1-(1,4-Dioxo-3-oxopent-1-yl)-phen-2-yl)-5,15-bis(pentafluorophenyl)corrole] 3.\textsuperscript{2} Corresponding aldehyde 1 (420 mg, 2.21 mmol, 1 eq.) and pentafluorophenylidipyrrromethane 2 (1.47 mg, 4.68 mmol, 2.1 eq.) were reacted in methanol (220 mL) in the presence of 2% HCl\textsubscript{aq} (220 mL) for 1.5 hour at the room temperature. The reaction mixture was then extracted with CHCl\textsubscript{3} (3 x 100 mL). Combined organic layers were washed with water (2 x 50 mL), dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, filtered and diluted with CHCl\textsubscript{3} to the volume of 500 mL. Subsequently, to the resulting mixture, a solution of DDQ (1.41 g, 2.61 mmol) in toluene (400 mL) was added and stirred for an additional 15 minutes. After evaporation to dryness, the crude product was purified by dry column vacuum chromatography (DCVC) (silica, hexanes, then CH\textsubscript{2}Cl\textsubscript{2}/hexanes, 30:70) and crystallized from hexanes to give analytically pure dark purple crystals of 3 (0.94 g, 54% yield); Rf 0.44 (silica, hexane/ethyl acetate, 4:1); \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): δH(ppm) = 9.06 (d, 2H, J = 4.0 Hz, β-H), 8.68 (bs, 4H, β-H), 8.53 (bs, 2H, β-H), 7.98 (d, 1H, J = 7.0 Hz, Ph), 7.73-7.70 (m, 1H, Ph), 7.40-7.37 (m, 1H, Ph), 7.16 (d, 1H, J = 8.0 Hz, Ph), 4.36 (s, 2H, CH\textsubscript{2}), 3.47 (s, 3H, CH\textsubscript{3}), -2.53 (bs, 3H, NH); HRMS (ESI) [M+H]\textsuperscript{+} Calcd: 795.1454 for C\textsubscript{40}H\textsubscript{21}F\textsubscript{10}N\textsubscript{4}O\textsubscript{3}, observed 795.1431, isotope profiles agreed.

**General Procedure for the Preparation of Corrole Amides.** Parent corrole 3 (0.5 mmol, 1 eq.), corresponding amine (7.5 mmol, 15 eq.) and DBU (0.25 mmol, 0.5 eq.) were dissolved in the mixture of toluene (18 mL) and methanol (2 mL). The resulting solution was protected from sunlight and stirred at room temperature for 7 days. The reaction mixture was then poured into water (50 mL) and extracted with CH\textsubscript{2}Cl\textsubscript{2} (2 x 50 mL). Organic layers were combined, dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, filtered and concentrated \textit{in vacuo}. The purification of each compound is described as follows.

10-[(N-(2-Hydroxyethyl)carbamoylmethoxy)phenyl]-5,15-bis(pentafluorophenyl)corrole] 7. Following the general procedure, corrole 3 and amine 4 were reacted. The crude reaction mixture was purified by means of DCVC (silica, CH\textsubscript{2}Cl\textsubscript{2}, then methanol/CH\textsubscript{2}Cl\textsubscript{2}, 1:99) and crystallized from hexanes giving dark purple crystals of 7
Following the general procedure, corrole 3 and amine 5 were reacted. The crude reaction mixture was purified by means of DCVC (silica, CH$_2$Cl$_2$, then methanol/CH$_2$Cl$_2$, 1:99) and crystallized from hexanes giving dark purple crystals of 8 (0.38 g, 87% yield); X-ray diffraction suitable crystals were grown by vapor diffusion of hexane into a concentrated solution of corrole in CHCl$_3$ at room temperature; $R'f$ 0.42 (silica, methanol/CH$_2$Cl$_2$, 2:98); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$(ppm) = 9.00 (d, 2H, J = 4.5 Hz, $\beta$-H), 8.61 (d, 2H, J = 4.5 Hz, $\beta$-H), 8.55 (d, 2H, J = 4.5 Hz, $\beta$-H), 8.42 (d, 2H, J = 4.0 Hz, $\beta$-H), 7.92 (dd, 1H, J$_1$ = 7.5 Hz, J$_2$ = 1.5 Hz, Ph), 7.78 – 7.75 (m, 1H, Ph), 7.42 – 7.39 (m, 1H, Ph), 7.30 (d, 1H, J = 8.0 Hz, Ph), 6.26 (d, 1H, J = 8.0 Hz, Py), 5.77 (dd, 1H, J$_1$ = 7.3 Hz, J$_2$ = 5.0 Hz, Py), 5.35-5.34 (m, 1H, Py), 5.15-5.13 (m, 1H, Ph), 4.52 (s, 2H, C(O)CH$_2$), 3.27 (s, 3H, NHCH$_2$ and NH-), -0.60 (bs, 3H, NH-corrole); HRMS (ESI) [M+H]$^+$ Calcd: 871.1879 for C$_{43}$H$_{28}$F$_{10}$N$_5$O$_2$, observed 871.1852, isotope profiles agreed.

Following the general procedure, corrole 3 and amine 6 were reacted. The crude reaction mixture was purified by means of DCVC (silica, CH$_2$Cl$_2$, then methanol/CH$_2$Cl$_2$, 0.5:99.5) and crystallized from hexanes, giving dark purple crystals of 9 (0.35 g, 84% yield); X-ray diffraction suitable crystals were grown by vapor diffusion of hexane into a concentrated solution corrole in CHCl$_3$ at room temperature; $R'f$ 0.56 (silica, hexane/ethyl acetate, 3:2); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$(ppm) = 9.12 (d, 2H, J = 4.5 Hz, $\beta$-H), 8.70 (d, 2H, J = 4.5 Hz, $\beta$-H), 8.62 (d, 2H, J = 4.5 Hz, $\beta$-H), 8.58 (bs, 2H, $\beta$-H), 8.06 (dd, 1H, J$_1$ = 7.0 Hz, J$_2$ = 1.5 Hz, Ph), 7.78 (m, 1H, Ph), 7.46 (m, 1H, Ph), 7.25 (m, 1H, Ph), 4.66 (s, 1H, NH), 4.29 (s, 2H, C(O)CH$_2$), 2.13-2.10 (m, 2H, NHCH$_2$), -0.26 – -0.32 (m, 4H, CH$_2$CH$_2$), -0.48 (t, 3H, J = 7.0 Hz, CH$_3$), -3.17 (bs, 3H, NH-corrole); HRMS (ESI) [M+H]$^+$ Calcd: 836.2083 for C$_{43}$H$_{28}$F$_{10}$N$_5$O$_2$, observed 836.2065, isotope profiles agreed.
2. **Photophysics.** Absorption spectra of dilute toluene (TOL), acetonitrile (ACN), dichloromethane (DCM) and methanol (MeOH) solutions for the determination of the absorption coefficients were obtained using PerkinElmer Lambda 950 UV/VIS/NIR spectrophotometer. Steady-state photoluminescence spectra were measured in air-equilibrated and de-aerated (by bubbling Ar) solutions at room temperature using an Edinburgh FLS920 fluorimeter, equipped with a Peltier-cooled R928 (200-850 nm) Hamamatsu PMT. Luminescence quantum yields at room temperature were evaluated by comparing wavelength integrated intensities of the corrected emission spectra with reference to tetraphenyl porphyrin (\( \phi = 0.11 \) in air-equilibrated toluene).\(^4\) The concentration was adjusted to obtain absorbance values of \( A \leq 0.1 \) at the excitation wavelengths. Luminescence measurements at 77 K were performed by employing quartz capillary tubes immersed in liquid nitrogen and hosted within a homemade quartz cold finger Dewar apparatus. Band maxima and relative luminescence intensities are obtained with uncertainties of 2 nm and 10%, respectively.

Luminescence lifetimes were obtained using a Jobin-Yvon IBH 5000F TCSPC apparatus equipped with a TBX Picosecond Photon Detection Module and NanoLED pulsed excitation sources (\( \lambda_{\text{exc}} = 373 \) nm). Analysis of the luminescence decay profiles over time was accomplished using the Decay Analysis Software DAS6 provided by the manufacturer. The lifetime values were obtained with an estimated uncertainty of 10%.
Figure S1. Absorption and emission (normalized for the quantum yield) spectra of corroles 3, 7 and 9 in toluene (TOL) at room temperature.
Figure S2. Absorption and emission (normalized for the quantum yield) spectra of corroles 3, 7 and 9 in acetonitrile (ACN) at room temperature.
Figure S3. Absorption and emission (normalized for the quantum yield) spectra of corroles 3, 7 and 9 in dichloromethane (DCM) at room temperature.
Figure S4. Absorption and emission (normalized for the quantum yield) spectra of corroles 3, 7 and 9 in methanol (MeOH) at room temperature.
Figure S5. Normalised emission spectra of corroles 3, 7 and 9 in toluene (TOL) at 77 K.
Figure S6. Absorption spectra of 3 in MeOH:H₂O solution (water % from 0, blue line, to 80, red line), c = 8.0 × 10⁻⁶ M.
Figure S7. Absorption spectra of 7 in MeOH:H₂O solution (water % from 0, blue line, to 80, red line), $c = 7.3 \times 10^{-6}$ M.
Figure S8. Absorption spectra of 9 in MeOH:H$_2$O solution (water % from 0, blue line, to 80, red line), $c = 7.0 \times 10^{-6}$ M.
Figure S9. Absorption variation at $\lambda = 406$ nm of 3, 7 and 9 in MeOH:H$_2$O solution.
Figure S10. Emission spectra of 3 in MeOH:H$_2$O solution.
Figure S11. Emission spectra of 7 in MeOH:H₂O solution.
Figure S12. Emission spectra of 9 in MeOH:H₂O solution.
Table S1. Absorption features of corroles 3, 7 and 9 in TOL, ACN, DCM and MeOH.

<table>
<thead>
<tr>
<th></th>
<th>TOL</th>
<th>ACN</th>
<th>DCM</th>
<th>MeOH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{max}}$, nm</td>
<td>$\lambda_{\text{max}}$, nm</td>
<td>$\lambda_{\text{max}}$, nm</td>
<td>$\lambda_{\text{max}}$, nm</td>
</tr>
<tr>
<td></td>
<td>($\varepsilon_{\text{max}}$, M$^{-1}$cm$^{-1}$)</td>
<td>($\varepsilon_{\text{max}}$, M$^{-1}$cm$^{-1}$)</td>
<td>($\varepsilon_{\text{max}}$, M$^{-1}$cm$^{-1}$)</td>
<td>($\varepsilon_{\text{max}}$, M$^{-1}$cm$^{-1}$)</td>
</tr>
<tr>
<td>3</td>
<td>416 (119,000)</td>
<td>417 (123,000)</td>
<td>408 (137,500)</td>
<td>406 (133,400)</td>
</tr>
<tr>
<td></td>
<td>565 (20,700)</td>
<td>566 (18,800)</td>
<td>559 (22,500)</td>
<td>565 (23,400)</td>
</tr>
<tr>
<td></td>
<td>615 (12,700)</td>
<td>619 (19,700)</td>
<td>611 (15,300)</td>
<td>611 (16,700)</td>
</tr>
<tr>
<td>7</td>
<td>413 (127,700)</td>
<td>410 (125,100)</td>
<td>409 (142,700)</td>
<td>409 (130,000)</td>
</tr>
<tr>
<td></td>
<td>570 (22,800)</td>
<td>567 (20,100)</td>
<td>567 (23,900)</td>
<td>567 (21,200)</td>
</tr>
<tr>
<td></td>
<td>615 (14,800)</td>
<td>617 (18,900)</td>
<td>611 (15,300)</td>
<td>614 (18,600)</td>
</tr>
<tr>
<td>9</td>
<td>415 (106,900)</td>
<td>419 (107,900)</td>
<td>409 (122,800)</td>
<td>408 (109,100)</td>
</tr>
<tr>
<td></td>
<td>567 (17,500)</td>
<td>565 (16,400)</td>
<td>559 (19,700)</td>
<td>566 (17,200)</td>
</tr>
<tr>
<td></td>
<td>615 (11,000)</td>
<td>620 (15,300)</td>
<td>611 (11,800)</td>
<td>614 (15,200)</td>
</tr>
</tbody>
</table>

Table S2. Luminescence properties of corroles 1, 2 and 3 in TOL, ACN, DCM and MeOH at room temperature.$^a$

<table>
<thead>
<tr>
<th></th>
<th>TOL</th>
<th>ACN</th>
<th>DCM</th>
<th>MeOH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{max}}$, nm</td>
<td>$\phi$, $\tau$, ns</td>
<td>$\lambda_{\text{max}}$, nm</td>
<td>$\phi$, $\tau$, ns</td>
</tr>
<tr>
<td>3</td>
<td>650, 619</td>
<td>0.155, 4.0</td>
<td>648, 619</td>
<td>0.150, 3.8</td>
</tr>
<tr>
<td></td>
<td>710 sh</td>
<td>(0.169)</td>
<td>(5.3)</td>
<td>700 sh</td>
</tr>
<tr>
<td>7</td>
<td>650, 618</td>
<td>0.156, 3.8</td>
<td>650, 618</td>
<td>0.154, 3.8</td>
</tr>
<tr>
<td></td>
<td>710 sh</td>
<td>(0.160)</td>
<td>(5.5)</td>
<td>700 sh</td>
</tr>
<tr>
<td>9</td>
<td>650, 621</td>
<td>0.154, 4.3</td>
<td>650, 621</td>
<td>0.140, 3.8</td>
</tr>
<tr>
<td></td>
<td>710 sh</td>
<td>(0.165)</td>
<td>(5.5)</td>
<td>700 sh</td>
</tr>
</tbody>
</table>

$^a$ In air-equilibrated (de-aerated) solutions; $\lambda_{\text{exc}} = 560$ nm, for quantum yield determination, and $\lambda_{\text{exc}} = 373$ nm, for lifetime measurements.

Table S3. Luminescence properties of corroles 3, 7 and 9 in DCM:MeOH, ACN, DCM and MeOH at 77 K.$^a$

<table>
<thead>
<tr>
<th></th>
<th>DCM:MeOH (1:1)</th>
<th>ACN</th>
<th>DCM</th>
<th>MeOH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{max}}$, nm</td>
<td>$\tau$, ns</td>
<td>$\lambda_{\text{max}}$, nm</td>
<td>$\tau$, ns</td>
</tr>
<tr>
<td>3</td>
<td>619, 619</td>
<td>6.5</td>
<td>632, 619</td>
<td>0.7, 6.3</td>
</tr>
<tr>
<td></td>
<td>(30:70)</td>
<td>(50:50)</td>
<td>(50:50)</td>
<td>(50:50)</td>
</tr>
<tr>
<td>7</td>
<td>618, 619</td>
<td>5.7</td>
<td>616, 619, 656</td>
<td>0.8, 4.7</td>
</tr>
<tr>
<td></td>
<td>(50:50)</td>
<td>(40:60)</td>
<td>(40:60)</td>
<td>(40:60)</td>
</tr>
<tr>
<td>9</td>
<td>621, 621</td>
<td>6.5</td>
<td>618, 621</td>
<td>1.2, 5.4</td>
</tr>
<tr>
<td></td>
<td>(50:50)</td>
<td>(50:50)</td>
<td>(50:50)</td>
<td>(50:50)</td>
</tr>
</tbody>
</table>

$^a$ $\lambda_{\text{max}}$ values from uncorrected spectra; $\lambda_{\text{exc}} = 373$ nm, for lifetime measurements.
Table S4. Luminescence properties of corroles 3, 7 and 9 in MeOH:H₂O (v:v) at room temperature.\textsuperscript{a}

<table>
<thead>
<tr>
<th>MeOH:H₂O</th>
<th>3</th>
<th>7</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>λ&lt;sub&gt;max&lt;/sub&gt;, nm</td>
<td>τ, ns</td>
<td>λ&lt;sub&gt;max&lt;/sub&gt;, nm</td>
</tr>
<tr>
<td>100:0</td>
<td>654</td>
<td>3.4</td>
<td>654</td>
</tr>
<tr>
<td>80:20</td>
<td>654</td>
<td>3.4</td>
<td>654</td>
</tr>
<tr>
<td>50:50</td>
<td>654</td>
<td>3.2</td>
<td>654</td>
</tr>
</tbody>
</table>

\textsuperscript{a} In air-equilibrated solutions; \( \lambda_{\text{exc}} = 560 \) nm, for emission spectra, and \( \lambda_{\text{exc}} = 373 \) nm, for lifetime measurements; n.d. is not detected.
Figure S13. Hydrogen bonded sheets of corrole 9.
Figure S14. Crystal structure of 8·CHCl₃ showing intramolecular π-π interactions between the pyridine side chain and the macrocyclic core as well as the hydrogen bonded helical assembly of 8. Hydrogen atoms removed for clarity.
Figure S15. Crystal structure of 8·CHCl₃ showing intramolecular π-π interactions between the pyridine side chain and the macrocyclic core – another view.
Data Collected on:
nmrvar-nmr4300
Archive directory:
Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Aug 29 2013

Temp. 25.0 C / 298.1 K
Operator: nmr2

Relax. delay 0.001 sec
Pulse 45.0 degrees
Avg. time 2.045 sec
Width 11061.9 Hz
16 repetitions
OBSERVE H1, 499.9309622 MHz
DATA PROCESSING
FT size 65536
Total time 0 min 25 sec
Data Collected on:
mmrvar-nmr5500
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pol)
Solvent: cdcl3
Data collected on: Feb 13 2014

Temp. 25.0 C / 298.1 K
Operator: vnr2

Relax. delay 0.001 sec
Pulse 45.0 degrees
Acq. time 2.045 sec
Width 11061.9 Hz
16 repetitions

OBSERVE H1, 499.9309619 MHz
DATA PROCESSING
FT size 65536
Total time 0 min 25 sec

14 12 10 8 6 4 2 0 -2 ppm
5.94 3.25 3.21 3.22 8.20
18.53 3.16 6.75 7.95 10.00
Data Collected on:
neuren-vmm500
Archive directory:

Sample directory:

FidFile: PROTON
Pulse Sequence: PROTON (e2pul)
Solvent: cdcl3
Data collected on: Feb 14 2014

Temp. 25.0 C / 298.1 K
Operator: vmm2

Relax. delay 0.001 sec
Pulse 45.0 degrees
Acq. time 2.045 sec
Width 9842.5 Hz
32 repetitions
OBSERVE K, 499.9309616 MHz
DATA PROCESSING
FT size 65536
Total time 0 min 25 sec

![NMR Spectrogram](image)
REFERENCES


