Intramolecular Energy and Electron Transfer
Within a Diazaperopyrenium-Based Cyclophane

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1. Materials / General Methods / Instrumentation

All reagents were purchased from commercial suppliers and used without further purification unless stated otherwise. Commercial grades of anhydrous solvents were deoxygenated by passing Ar through the solvent for 30 min. $^1$ and $^2$ (see Scheme S1 for their structural formulas) and $^{ExBIPY}$ (see Scheme S4 for its structural formula) were synthesized based on previous literature procedures.$^{1-3}$ Analytical high-performance liquid chromatography (HPLC) was performed on reverse-phase HPLC (RP-HPLC) instruments, using a C$_{18}$-column and a binary solvent system (MeCN and H$_2$O with 0.1% CF$_3$COOH). Column chromatography was carried out on silica gel 60F (Merck 9385, 0.040–0.063 mm). UV/Vis Absorbance spectra were recorded using a UV-3600 Shimadzu spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded on an Agilent 500 MHz spectrometer with working frequencies of 500 MHz ($^1$H NMR) and 125 MHz ($^{13}$C NMR). Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvents (CD$_3$CN: δ$_H$ = 1.94 ppm and δ$_C$ = 1.32 ppm; CDCl$_3$: δ$_H$ = 7.26 ppm CD$_3$SOCD$_3$: δ$_H$ = 2.50 ppm and δ$_C$ = 39.52 ppm). High-resolution mass spectra (HRMS) were measured on an Agilent 6210 Time-of-Flight (TOF) LC-MS, using an ESI source, coupled with Agilent 1100 HPLC stack, using direct infusion (0.6 mL min$^{-1}$). Cyclic voltammetry (CV) experiments were carried out at room temperature in an Ar-purged solution in DMF with a Gamry Multipurpose instrument (Reference 600) interfaced to a PC. All CV experiments were performed using a glassy carbon working electrode (0.071 cm$^2$). The electrode surface was polished routinely with 0.05 μm alumina-water slurry on a felt surface immediately before use. The counter electrode was a Pt coil and the reference electrode was a Ag/AgCl electrode. Tetrabutylammonium hexafluorophosphate (TBAPF$_6$) solution (0.1 M) in DMF was used as supporting electrolyte.

Steady-state and time-resolved emission spectra were acquired using HORIBA Fluorolog-3 equipped with a TCSPC module (diode laser excitation at λ = 375 nm) and an integrating sphere was used for absolute photoluminescence quantum yield determination. Picosecond time-resolved fluorescence measurements were made using a commercial direct-diode-pumped 100 kHz amplifier (Spirit 1040-4, Spectra-Physics), which produced the fundamental beam of 1,040 nm (350 fs, 4.5W) used to pump a non-collinear optical parametric amplifier (Spirit-NOPA, Spectra-Physics) which delivered tunable, high-repetition-rate pulses with pulse widths as short as sub-20 fs. The DAPPBox$^{4+}$ sample was excited with 340 nm, 2 nJ laser pulses. Fluorescence was detected using a Hamamatsu C4780 Streakscope as previously described.$^4$ Samples were prepared in 2 mm quartz cuvettes. All data were acquired in the single-photon-counting mode using the Hamamatsu.
HPD-TA software. The temporal resolution was approximately 2% of the sweep window. Single wavelength kinetic analysis was performed using a nonlinear least-squares fit to a sum of exponentials convoluted with an instrument response function.

Visible and near-infrared femtosecond and nanosecond transient absorption spectroscopies (fsTA\textsuperscript{5} and nsTA,\textsuperscript{6} respectively) were performed using previously described instruments. The 330 nm, ~60 fs pump pulses were generated at 1\mu J per pulse using a commercial non-collinear optical parametric amplifier (TOPAS-White, Light-Conversion, Ltd.). The pump polarization was randomized using a commercial depolarizer (DPU-25-A, Thorlabs, Inc.) to eliminate any orientational dynamics contributions from the experiment. Spectra were collected on commercial spectrometers for each time window (customized Ultrafast Systems Helios and EOS spectrometers, for fsTA and nsTA, respectively). All samples were stirred to avoid localized heating or degradation effects. The optical density was maintained at 0.6 for all samples.

All transient absorption data were background-subtracted to remove scattered light and thermally lensed fluorescence from the spectra, and then corrected for group delay dispersion (GDD, or "chirp") using Surface Xplorer Pro 4 (Ultrafast Systems, LLC). The kinetic analysis was performed using home written programs in MATLAB\textsuperscript{7} and was based on a global fit to selected single-wavelength kinetics. The time-resolution is given as $\tau = 250$ fs (full width at half maximum, FWHM); the assumption of a uniform instrument response across the frequency domain and a fixed time-zero ($t_0$) are implicit in global analysis.

The kinetic data from multiple different wavelengths are fit using the global analysis described below. Each wavelength is given an initial amplitude that is representative of the spectral intensity at time $t_0$, and varied independently to fit the data. The time/rate constants and $t_0$ are shared between the various kinetic data and are varied globally across the kinetic data in order to fit the model(s) described below. We globally fit the dataset to a specified kinetic model and use the resultant populations to deconvolute the dataset and reconstruct species-associated spectra.

We used the following first-order kinetic models with rate matrices $K$ for the compounds and excitation wavelengths:
For the fsTA of **Me-DAPP**\(^{2+}\), **Bn-DAPP**\(^{2+}\), and **DAPPBox**\(^{4+}\) exciting at 505 nm:

\[
K = \begin{pmatrix}
-k_{\text{relax}} & 0 & 0 \\
k_{\text{relax}} & -k_{S1} & 0 \\
0 & k_{S1} & 0
\end{pmatrix}
\] 

(Eqn. S1)

For the fsTA of **Me-DAPP**\(^{2+}\), **Bn-DAPP**\(^{2+}\) at 505, 414, and 330 nm, and **DAPPBox**\(^{4+}\) exciting at 414 nm:

\[
K = \begin{pmatrix}
-k_{IC} & 0 & 0 & 0 \\
k_{IC} & -k_{\text{relax}} & 0 & 0 \\
0 & k_{\text{relax}} & -k_{S1} & 0 \\
0 & 0 & k_{S1} & 0
\end{pmatrix}
\] 

(Eqn. S2)

For the fsTA of **Bn-ExBIPY**\(^{2+}\) exciting at 330 nm:

\[
K = \begin{pmatrix}
-k_{FeT} & 0 & 0 \\
k_{FeT} & -k_{BeT} & 0 \\
0 & k_{BeT} & 0
\end{pmatrix}
\] 

(Eqn. S3)

For the fsTA of **DAPPBox**\(^{4+}\) exciting at 330 nm (for simplicity, no explicit triplet population was considered; equal initial state populations were also assumed):

\[
K = \begin{pmatrix}
-k_{EnT} & 0 & 0 & 0 & 0 \\
k_{EnT} & -k_{\text{relax}} & 0 & 0 & 0 \\
0 & k_{\text{relax}} & -k_{S1} & 0 & 0 \\
0 & 0 & 0 & -k_{FeT} & 0 \\
0 & 0 & 0 & k_{FeT} & -k_{BeT}
\end{pmatrix}
\] 

(Eqn. S4)

For the nsTA of **Me-DAPP**\(^{2+}\), **Bn-DAPP**\(^{2+}\) exciting at 505 nm, 414 nm and 330 nm, and **DAPPBox**\(^{4+}\) exciting at 505 nm and 414 nm (for simplicity, the triplet decay in air-equilibrated solution was modeled as a unimolecular decay):
\[
K = \begin{pmatrix}
-k_{s1} & 0 \\
 k_{s1} & -k_T \\
\end{pmatrix}
\]

(Eqn. S5)

For the nsTA of DAPPBox\textsuperscript{4+} exciting at 330 nm (for simplicity, the triplet decay in air-equilibrated solution was modeled as a unimolecular decay; equal initial state populations were also assumed; precise differences in initial population are encoded in the different \(\Delta A\) amplitudes of the reconstructed species-associated spectra):

\[
K = \begin{pmatrix}
-k_{s1} & 0 & 0 \\
 k_{s1} & -k_T & 0 \\
0 & 0 & -k_{BeT} \\
\end{pmatrix}
\]

(Eqn. S6)

The MATLAB program numerically the solves the differential equations through matrix methods,\textsuperscript{8} then convolutes the solutions with a Gaussian instrument response function with width \(w\) (FWHM), before employing a least-squares fitting using a Levenberg-Marquardt or Simplex method to find the parameters which result in matches to the kinetic data.

Once the fit parameters are established, they are fed directly into the differential equations, which were solved for the populations of the states in model—i.e., \(A(t)\), \(B(t)\), \(C(t)\), and \(D(t)\). Finally, the raw data matrix (with all the raw data) is deconvoluted with the populations as functions of time to produce the spectra associated with each species.

2. Synthetic Protocols

<table>
<thead>
<tr>
<th>Scheme S1. Synthesis of 3 from 1 and 2</th>
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\(\text{New Method}\)  
\(\text{Me}_2\text{SO} / \text{RT} / 5\ h\)  
\(85\%\)  
\(\text{Old Method}\)  
\(\text{THF} / \text{RT} / 3\ d\)  
\(\text{Not Isolated}\)
3: $2^2$ (622.5 mg, 4.53 mmol) was added with stirring to a solution of $1^1$ (135 mg, 0.302 mmol) in Me$_2$SO (8 mL) at room temperature. See Scheme S1. After 5 h, deionized H$_2$O (100 mL) was added to the reaction mixture, resulting in the formation of a dark yellow precipitate, which was filtered off, washed with deionized H$_2$O and a small amount of EtOH, before being dried under vacuum to afford (147 mg, 85 %) a dark yellow solid 3. $^1$H NMR (500 MHz, CD$_3$SOCD$_3$): $\delta_H = 8.20$ (d, $J = 7.7$ Hz, 4H), 7.32 (q, $J = 8.0$ Hz, 8H), 7.24 (d, $J = 7.7$ Hz, 4H), 4.50 (d, $J = 5.7$ Hz, 4H), 3.86 (s, 8H), 3.75 (s, 4H) ppm. $^{13}$C NMR (126 MHz, CD$_3$SOCD$_3$): $\delta_C = 140.8, 135.7, 132.7, 128.1, 125.1, 122.6, 119.1, 62.1, 60.3, 55.2$ ppm. The product was used without further purification in the next step. It is assumed that the poor solubility of 1 and 3 in common organic solvents like CH$_2$Cl$_2$, MeCN and Me$_2$CO — and even in tetrahydrofuran (THF) — is the main reason that the yield of the reaction is low. It is more than likely that, after one 'end' of 1 has reacted with 1 equiv of 2, the intermediate precipitates from the solvent and so is not available in the mixture to continue and complete the reaction and form the final product 3. What makes the situation even more challenging is the fact that the poor solubilities of the intermediate and the desired final product make it far from easy to isolate them. This rationalization might provide the explanation why, in the previous literature,$^1$ the experimentalists proceed to the next oxidation step of the DAPP$^{2+}$ preparation without isolating the product at this point. The use of Me$_2$SO as the solvent results in the starting material 1, the intermediate and product 3 all being much more soluble and so it follows that the yield of 3 will be much larger as a result. Also, this polar aprotic solvent tends to favor these S$_N$2 reactions. Based on the above analysis, it is not surprising that a change of solvent, not only leads to a much better yield, but also shortens considerably the reaction time from 3 d to 5 h.

![Scheme S2. Synthesis of 4•2PF$_6$ from 3](image)

4•2PF$_6$: DDQ (240 mg, 1.057 mmol) was added to a dark yellow solution of 3 (100 mg, 0.182 mmol) in DMF (8 mL) at room temperature. See Scheme S2. The color of the reaction mixture became dark brown upon the addition of the DDQ. After stirring for 8 h, a satd aqueous solution
(100 mL) of NH₄PF₆ was added to the reaction mixture. The resulting precipitate was filtered off, washed with deionized H₂O and a small amount of EtOH, before being dried under vacuum to afford (138 mg, 90 %) a dark brown solid 4•2PF₆. The crude product was dissolved in MeCN to exchange the anion from PF₆⁻ to Cl⁻ by addition of an excess of tetrabutylammonium chloride (TBACl). The crude dichloride was then subjected to reverse-phase HPLC, starting with H₂O / 0.1 % TFA as eluent and adding up to 100 % of MeCN / 0.1% TFA to the eluent within 40 min. The pure fractions were collected and concentrated under vacuum. The residue was dissolved in H₂O, followed by the addition of NH₄PF₆ to yield pure 4•2PF₆ (124 mg, 80 %). ¹H NMR (500 MHz, CD₃SOCD₃): δH = 10.39 (s, 4H), 9.94 (s, 4H), 8.95 (s, 4H), 7.72 (d, J = 7.9 Hz, 4H), 7.45 (d, J = 7.8 Hz, 4H), 6.41 (s, 4H), 4.53 (s, 4H) ppm. ¹³C NMR (126 MHz, CD₃SOCD₃): δC = 150.4, 138.4, 128.3, 128.3, 126.5, 126.2, 113.7, 100.3, 61.8 ppm.

BrDAPP•2PF₆: 4•2PF₆ (100 mg, 0.116 mmol) was dissolved in MeCN (15 mL) and PBr₃ (100 μL, 1.063 mmol) was added slowly while stirring at room temperature overnight. See Scheme S3.

A satd aqueous solution (100 mL) of NH₄PF₆ was added to quench the reaction, resulting in the formation of a reddish brown solid. The resulting precipitate was filtered off, washed with deionized H₂O and a small amount of EtOH, before being dried under vacuum to afford (80 mg, 70 %) a reddish brown solid BrDAPP•2PF₆. ¹H NMR (500 MHz, CD₃SOCD₃): δH = 10.44 (s, 4H), 10.04 (d, J = 9.6 Hz, 4H), 9.04 (d, J = 9.3 Hz, 4H), 7.72 (d, J = 7.9 Hz, 4H), 7.60 (d, J = 8.0 Hz, 4H), 6.45 (s, 4H), 4.74 (s, 4H) ppm. ¹³C NMR (126 MHz, CD₃SOCD₃): δC = 161.7, 138.8, 129.5, 128.7, 127.7, 127.2, 126.1, 63.7, 39.0, 33.0 ppm.
**DAPPBox•4PF₆**: Four different reactions were carried out in order to establish the best conditions for the ring-closing step. 1) *No template and no catalyst*; 2) *Template without a catalyst*; 3) *Template and a catalyst*; 4) *Catalyst without a template*.

(1) *No template and no catalyst*. A solution of BrDAPP•2PF₆ (50 mg, 0.05 mmol), ExBIPY³ (11 mg, 0.05 mmol) in dry MeCN (20 mL) was stirred at room temperature for 20 days. Excess of TBACl was added to quench the reaction and the resulting crude precipitate was then subjected to reverse-phase HPLC preparative C₁₈ column chromatography, starting with H₂O / 0.1 % TFA as eluent, and adding up to 100 % of MeCN / 0.1% TFA as eluent during 45 min. The pure fractions were collected and concentrated under vacuum. The residue was dissolved in H₂O, followed by the addition of NH₄PF₆ to yield pure DAPPBox•4PF₆ in trace amounts.

(2) *Pyrene as a Template without Catalyst*. A solution of BrDAPP•2PF₆ (1 equiv), ExBIPY (1 equiv) and pyrene (6 equiv) in dry MeCN was stirred at room temperature for 7 days. See Scheme S4. Excess of TBACl was added to quench the reaction and the resulting crude precipitate was then dissolved in H₂O and the pyrene template was removed by continuous liquid-liquid extraction with CHCl₃ and H₂O during 3 days. The aqueous phase was concentrated to a small volume and then subjected to reverse-phase HPLC, starting with H₂O / 0.1 % TFA as eluent, and adding up to 100 % of MeCN / 0.1% TFA as eluent within 45 min. The pure fractions were collected and
concentrated in vacuum. The residue was dissolved in H$_2$O, followed by the addition of NH$_4$PF$_6$ to afford pure DAPPBox•4PF$_6$ in 35 % yield. $^1$H NMR (500 MHz, CD$_3$CN): $\delta_{H} = 9.96$ (s, 4H), 9.65 (s, 4H), 8.86 (s, 4H), 8.65 (d, $J = 6.1$ Hz, 4H), 7.95 – 7.83 (m, 8H), 7.61 (d, $J = 8.0$ Hz, 4H), 7.54 (s, 4H), 6.28 (s, 4H), 5.62 (s, 4H) ppm. $^{13}$C NMR (126 MHz, CD$_3$CN): $\delta_{C} = 144.5$, 138.2, 130.8, 130.6, 129.3, 127.0, 126.0, 66.4, 64.5 ppm. HRMS (ESI) for DAPPBox•4PF$_6$; Calcd for C$_{56}$H$_{40}$F$_{24}$N$_{4}$P$_{4}$: m/z = 1203.2174 [M – PF$_6$]$^+$; Found : 1203.2173 [M – PF$_6$]$^+$; 529.1266 [M – 2PF$_6$]$^{2+}$; Found : 529.1263 [M – 2PF$_6$]$^{2+}$; 304.4293 [M – 3PF$_6$]$^{3+}$; Found : 304.4293 [M – 3PF$_6$]$^{3+}$.

(3) Pyrene as a Template and TBAI as a Catalyst. A solution of BrDAPP•2PF$_6$ (1 equiv), ExBIPY (1 equiv), pyrene (6 equiv) and TBAI (0.2 equiv) in dry MeCN was stirred at 80 °C for 4 days. Excess of TBACl was added to quench the reaction and the resulting crude precipitate was then dissolved in H$_2$O in order to remove the pyrene template by continuous liquid-liquid extraction with CHCl$_3$ over 3 days. The resultant aqueous phase was concentrated to a small volume and then subjected to reverse-phase HPLC, starting with H$_2$O / 0.1 % TFA as eluent, and adding up to 100 % of MeCN / 0.1% TFA as eluent within 45 min. The pure fractions were collected and concentrated in vacuum. The residue was dissolved in H$_2$O, followed by the addition of NH$_4$PF$_6$ to afford pure DAPPBox•4PF$_6$ in 23 % yield.

(4) TBAI as a catalyst without a Template. A solution of BrDAPP•2PF$_6$ (1 equiv), ExBIPY (1 equiv), pyrene (6 equiv) and TBAI (0.2 equiv) in dry MeCN was stirred at 80 °C for 4 days. See Scheme S4. Excess of TBACl was added to quench the reaction and the resulting crude precipitated product was then subjected to reverse-phase HPLC, starting with H$_2$O / 0.1 % TFA as eluent, and adding up to 100 % of MeCN / 0.1% TFA as eluent within 45 min. The pure fractions were collected and concentrated in vacuum. The residue was dissolved in H$_2$O, followed by the addition of NH$_4$PF$_6$ to afford pure DAPPBox•4PF$_6$ in 20 % yield.
3. $^1$H NMR Spectroscopy

The 2D $^1$H NMR spectra of DAPPBox•4PF$_6$ are shown in Figure S1a, b.

Figure S1. $^1$H NMR Spectra (500 MHz, CD$_3$CN, 298 K) of DAPPBox•4PF$_6$. (a) $^1$H-$^1$H COSY NMR spectrum. (b) NOESY NMR spectrum.

Figure S2. $^1$H NMR Spectra (500 MHz, CD$_3$CN, 298 K). (a) Pyrene ⊂ DAPPBox•4PF$_6$. (b) DAPPBox•4PF$_6$. 
4. Host-Guest Studies of Complex of Pyrene $\subset$ DAPPBox$^{4+}$.

**Figure S3.** (a) Solid-state superstructure of complex of pyrene $\subset$ DAPPBox$^{4+}$. (b) A Job plot between the DAPPBox$^{4+}$ host and the pyrene guest, obtained by plotting the changes of the absorbance values of the cyclophane (MeCN, 298 K, 445nm) against the change in the mole fraction ($\chi_{\text{Pyrene}}$) of the guest. The total concentration of host and guest was maintained at 15 $\mu$M. The plot indicates a 1:1 binding between the host and guest. (c) The emission spectra of DAPPBox$^{4+}$ (3 $\mu$M in MeCN, 298 K, excited at 440nm) upon titration with the pyrene (up to 20 equiv) as the guest molecule (inset: Benesi-Hildebrand plot confirming the 1:1 stoichiometry). (d) Non-linear least square fitting curves of the fluorescence intensities vs the guest concentration. Binding constant $K_a$ [M$^{-1}$] for 1:1 complex, pyrene $\subset$ DAPPBox$^{4+}$, is $(3.73 \pm 0.35) \times 10^5$ M$^{-1}$. 
5. Crystallographic Characterization

(1) DAPPBox•4TFA (Figure S4)

Method. A 0.25 mM MeCN solution of DAPPBox•4TFA was filtered through a 0.45-µm syringe filter into VWR culture tubes. The culture tubes were placed in a closed 20-mL scintillation vial containing 3 mL iPr₂O. After 7 days, reddish brown crystals of DAPPBox•4TFA were obtained. A suitable crystal was selected and mounted in inert oil and transferred to the cold gas stream of a Bruker Kappa APEX CCD area detector diffractometer. The crystal was kept at 100 K during data collection. Using Olex2⁹, the structure was solved with the XM¹⁰ structure solution program using Dual Space and refined with the XL refinement package using Least Squares minimization.

Crystal Data for C₁₂₈H₈₀F₂₄N₈O₁₆, M = 2442.00, triclinic, space group P̅1 (no. 2), a = 13.3141(7), b = 21.1146(10), c = 23.4964(13) Å, α = 96.654(4), β = 99.661(4), γ = 105.932(4)°, V = 6169.5(6) Å³, Z = 2, T = 100 K, μ(CuKα) = 1.760 mm⁻¹. The final wR(F²) was 0.2377 (all data). Crystallographic data (excluding structure factors) for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC–1480961.

Refinement Details. All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints (except where required by crystallographic symmetry). Three of eight groups of the [CF₃COO]⁻ anions were disordered and were modeled over two positions using appropriate C–F and F–F distances (1.33 and 2.14 Å, respectively) of CF₃ groups in [CF₃COO]⁻ anions. The refinement was performed using several DFIX and ISOR constraints.

Solvent Treatment Details. Three of the eight CF₃ groups of the [CF₃COO]⁻ anions were disordered and were modeled over two positions using appropriate C–F and F–F distances. The residual electron density obtained after refinement of the cluster was diffuse but was successfully assigned to two disordered [CF₃COO]⁻ anions. These disordered [CF₃COO]⁻ anions were located on inversion centers after appropriate constraints.
Figure S4. Solid-state (super)structure of the DAPPBox⁴⁺ obtained from single-crystal X-ray diffraction. (a) Unit cell structure of DAPPBox⁴⁺. (b) Perspective view of the superstructure of DAPPBox⁴⁺.

(2) Pyrene ⊂ DAPPBox•4PF₆ (Figure S5)

Method. Pyrene was added in a 6 : 1 ratio to a 0.25 mM MeCN solution of DAPPBox•4PF₆ before being filtered through a 0.45-μm syringe filter into VWR culture tubes. The vial was placed in one closed 20-mL scintillation vial containing 3 mL iPr₂O. After 7 days, brown crystals of pyrene ⊂ DAPPBox•4PF₆ had formed. A suitable crystal was selected and mounted in inert oil and transferred to the cold gas stream of a Bruker Kappa APEX CCD area detector diffractometer. The crystal was kept at 99.99 K during data collection. Using Olex2⁹, the structure was solved with the XM¹⁰ structure solution program using Dual Space and refined with the XL refinement package using Least Squares minimization.

Crystal Data for complex of C₈₈H₆₇F₂₄N₈P₄, triclinic, space group P ̅ (no. 2), a = 10.7635(6), b = 11.6514(6), c = 17.8407(9) Å, α = 92.310(2), β = 106.077(2), γ = 102.044(2)°, V = 2091.08(19) Å³, Z = 1, T = 99.99 K, μ(CuKα) = 1.760 mm⁻¹, Dcalc = 1.442 g/mm³, 11494 reflections measured (5.184
≤ 2Θ ≤ 124.92), 6199 unique ($R_{int} = 0.0209$, $R_{sigma} = 0.0292$) which were used in all calculations. The final $R_1$ value was 0.1160 ($I > 2\sigma(I)$) and $wR_2$ was 0.3886 (all data). Crystallographic data (excluding structure factors) for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC–1431348.

**Refinement Details.** The occupancy of the free pyrene moiety was fixed at 0.25 based on the size of displacement parameters. The PF$_6^-$ anions were refined with similar distance restraints in order to maintain a spherical coordination environment about the central P atoms. The P atoms in the disordered PF$_6$ anions were refined with group anisotropic displacement parameters.

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**Figure S5.** Solid-state superstructure of the pyrene ⊂ DAPPBox•4PF$_6$ obtained from single-crystal X-ray diffraction. The complex is presented as stick representations with the corresponding semi-transparent space-filling representations superimposed upon them. (a) Perspective view of complex. (b) Plan view of the complex. (c) Complex viewed along $b$-axis.
6. Cyclic Voltammetry (CV) Experiments

The CV of DAPPBox$^{4+}$ in DMF shows (Figure S6) reduction peaks at $-0.58$, $-0.65$, $-0.77$ and $-1.20$ V. The peaks at $-0.65$ and $-0.77$ V are consistent with the reduction peaks of Bn-ExBIPY$^{2+}$ at $-0.58$ and $-1.20$ V and are assigned to two one-electron reductions of the DAPP$^{2+}$ unit. It should be noted that only the first redox process of DAPP$^{2+}$ unit is reversible. The lack of reversibility of the second reduction processes of DAPP$^{2+}$ unit probably results from 1) the decrease in the solubility of DAPPBox$^{4+}$PF$_6$ with its progressive loss of charge on reduction 2) the adsorption of the reduction product onto the electrode surface.\textsuperscript{11}

**Figure S6.** Cyclic voltammograms of the DAPPBox$^{4+}$ and the reference compounds (Bn-DAPP$^{2+}$ and Bn-ExBIPY$^{2+}$) in DMF (1.0 mM) recorded with a scan rate of 50 mV s$^{-1}$.

**Figure S7.** Cyclic voltammograms of the Bn-DAPP$^{2+}$ in MeCN (1.0 mM) recorded with a scan rate of 50 mV s$^{-1}$.
7. Photophysical Characterization

The detailed photophysical characterization experimental techniques have already been described in section 1 of this SI (General Method). See Figure S8 for the absorption spectra of the benzylated reference compounds (Bn-ExBIPY$^{2+}$ and Bn-DAPP$^{2+}$). See Figures S9 – S12 for the single wavelength monoexponential decay analysis, as well as the normalized steady-state absorption and emission spectra of DAPPBox$^{4+}$, Me-ExBIPY$^{2+}$, Me-DAPP$^{2+}$ and Bn-DAPP$^{2+}$, respectively. See Figure S13 to S21 for visible and NIR (a) fsTA and (b) nsTA spectra of Me-DAPP$^{2+}$, Bn-DAPP$^{2+}$ and Bn-ExBIPY$^{2+}$ in MeCN at room temp, respectively. See Figures S22 – S40 for the (a) multiple wavelength fits, (b) species associated spectra, and (c) population curves for the fsTA and nsTA data of Me-DAPP$^{2+}$, Bn-DAPP$^{2+}$, Bn-ExBIPY$^{2+}$, and DAPPBox$^{4+}$, respectively.

![Absorption Spectra](image)

**Figure S8.** Absorption spectra of Bn-ExBIPY$^{2+}$, Bn-DAPP$^{2+}$ as well as an equimolar ratio of physical mixture of Bn-ExBIPY$^{2+}$ and Bn-DAPP$^{2+}$ in MeCN at 298 K.
Figure S9. (a) Structural formula of DAPPBox$^{4+}$. (b) Time-resolved fluorescence spectrum of DAPPBox$^{4+}$PF$_6$ in MeCN (37 μM) upon excitation at 340 nm at 298 K. (c) Single wavelength (516 nm) analysis shows a fast rise, followed by a monoexponential (20 ns) decay of DAPPBox$^{4+}$PF$_6$. (d) Normalized steady-state absorption and emission for DAPPBox$^{4+}$PF$_6$ in MeCN, upon excitation at 395 nm at 298 K.

Figure S10. (a) Structural formula of Me-ExBIPY$^{2+}$. (b) Single wavelength (392 nm) analysis shows a monoexponential decay (1.56 ns) of Me-ExBIPY$^{2+}$. (c) Normalized steady-state absorption and emission of Me-ExBIPY$^{2+}$ in MeCN upon excitation at 320 nm at 298 K.
**Figure S11.** (a) Structural formula of Me-DAPP$^{2+}$. (b) Single wavelength (511 nm) analysis shows a monoexponential decay (17.5 ns) of Me-DAPP$^{2+}$. (c) Normalized steady-state absorption and emission of Me-DAPP$^{2+}$ in MeCN upon excitation at 320 nm at 298 K.

**Figure S12.** (a) Structural formula of Bn-DAPP$^{2+}$. (b) Single wavelength (508 nm) analysis shows a monoexponential decay (19.8 ns) of Bn-DAPP$^{2+}$. (c) Normalized steady-state absorption and emission of Bn-DAPP$^{2+}$ in MeCN upon excitation at 405 nm at 298 K.
Figure S13. Visible and NIR spectra. (a) fsTA (b) nsTA spectra for Me-DAPP$^{2+}$ in MeCN at room temp following a ~100 fs, 505 nm (1 μJ/pulse) excitation. Time delays for (a) and (b) are given in ps and ns, respectively.
Figure S14. Visible and NIR spectra. (a) fsTA (b) nsTA spectra for Me-DAPP$^{2+}$ in MeCN at room temp following a ~100 fs, 414 nm (1 μJ/pulse) excitation. Time delays for (a) and (b) are given in ps and ns, respectively.
Figure S15. Visible and NIR spectra. (a) fsTA (b) nsTA spectra for Me-DAPP$^{2+}$ in MeCN at room temp following a 60 fs, 330 nm (1 μJ/pulse) excitation. Time delays for (a) and (b) are given in ps and ns, respectively.
Figure S16. Visible and NIR spectra. (a) fsTA (b) nsTA spectra for Bn-DAPP$^{2+}$ in MeCN at room temp following a ~100 fs, 505 nm (1 μJ/pulse) excitation. Time delays for (a) and (b) are given in ps and ns, respectively.
Figure S17. Visible and NIR spectra. (a) fsTA (b) nsTA spectra for Bn-DAPP\(^{2+}\) in MeCN at room temp following a ~100 fs, 414 nm (1 \(\mu\)J/pulse) excitation. Time delays for (a) and (b) are given in ps and ns, respectively.
Figure S18. Visible and NIR spectra. (a) fsTA (b) nsTA spectra for Bn-DAPP$^{2+}$ in MeCN at room temp following a 60 fs, 330 nm (1 μJ/pulse) excitation. Time delays for (a) and (b) are given in ps and ns, respectively.
Figure S19. Visible and NIR spectra. (a) fsTA (b) nsTA spectra for DAPPBox$^{4+}$ in MeCN at room temp following a ~100 fs, 414 nm (1 μJ/pulse) excitation. Time delays for (a) and (b) are given in ps and ns, respectively.
Figure S20. Visible and NIR spectra nsTA spectra for DAPPBox$^{4+}$ in MeCN at room temp following a (a) 60 fs, 330 nm (1 μJ/pulse), or (b) ~100 fs, 505 nm (1 μJ/pulse) excitation. Time delays are given in ns
Figure S21. Visible and NIR fsTA spectra for Bn-ExBIPY\(^{2+}\) in MeCN at room temp following a 60 fs, 330 nm (1 μJ/pulse) excitation. Time delays are given in ps.
Figure S22. (a) Multiple wavelength fits and time constants from fsTA for the reference compound Me-DAPP$^{2+}$ excited at 505 nm. (b) Population curves fit to an A → B → C sequential decay model (Eqn. S1). (c) Species associated spectra. Species A represents the initially prepared singlet excited state ($^*S_1$), while species B is the structurally relaxed singlet excited state ($S_1$). The terminal species C is the triplet state seen in the nsTA, which appears at times longer than the time scale of this experiment.

Figure S23. (a) Multiple wavelength fits and time constants from fsTA for the reference compound Me-DAPP$^{2+}$ excited at 414 nm. (b) Population curves fit to an A → B → C→ D sequential decay model (Eqn. S2). (c) Species associated spectra. Species A represents the initially prepared singlet excited state ($S_2$), which internally converts (IC) to a hot/unrelaxed $^*S_1$ (species B). The lifetime of state A is close to the temporal resolution of the instrument, and so its spectrum is not fully deconvolved (represented as a dashed spectrum). This state then structurally relaxes to form the cooled $S_1$ state C. The terminal species D is the triplet state seen in the nsTA, which appears at times longer than the time scale of this experiment, so the spectrum of D is omitted.
Figure S24. (a) Multiple wavelength fits and time constants from fsTA for the reference compound Me-DAPP$^{2+}$ excited at 330 nm. (b) Population curves fit to an A $\rightarrow$ B $\rightarrow$ C $\rightarrow$ D sequential decay model (Eqn. S2). (c) Species associated spectra. Species A represents the initially prepared singlet excited state ($S_n$), which internally converts (IC) to a hot/unrelaxed *$S_1$ (species B). The lifetime of state A is close to the temporal resolution of the instrument, and so its spectrum is not fully deconvolved (represented as a dashed spectrum). This state then structurally relaxes to form the cooled $S_1$ state C. The terminal species D is the triplet state seen in the nsTA, which appears at times longer than the time scale of this experiment, so the spectrum of D is omitted. Our model was chosen for simplicity, so some of the IC/relaxation dynamics may remain convolved.

Figure S25. (a) Multiple wavelength fits and time constants from nsTA for the reference compound Me-DAPP$^{2+}$ excited at 505 nm. (b) Population curves fit to an A $\rightarrow$ B $\rightarrow$ GS (ground state) sequential decay model (Eqn. 5). (c) Species associated spectra. Species A represents the initially prepared singlet excited state, while species B is the triplet state.
Figure S26. (a) Multiple wavelength fits and time constants from nsTA for the reference compound Me-DAPP$^{2+}$ excited at 414 nm. (b) Population curves fit to an A → B → GS (ground state) sequential decay model (Eqn. S5). (c) Species associated spectra. Species A represents the initially prepared singlet excited state, while species B is the triplet state.

Figure S27. (a) Multiple wavelength fits and time constants from nsTA for the reference compound Me-DAPP$^{2+}$ excited at 330 nm. (b) Population curves fit to an A → B → GS (ground state) sequential decay model (Eqn. S5). (c) Species associated spectra. Species A represents the initially prepared singlet excited state, while species B is the triplet state.
Figure S28. (a) Multiple wavelength fits and time constants from fsTA for the reference compound Bn-DAPP$^{2+}$ excited at 505 nm. (b) Population curves fit to an A → B → C sequential decay model (Eqn. S1). (c) Species associated spectra. Species A represents the initially prepared singlet excited state ($^1S_1$), while species B is the structurally relaxed singlet excited state ($S_1$). The terminal species C is the triplet state seen in the nsTA, which appears at times longer than the time scale of this experiment.

Figure S29. (a) Multiple wavelength fits and time constants from fsTA for the reference compound Bn-DAPP$^{2+}$ excited at 414 nm. (b) Population curves fit to an A → B → C → D sequential decay model (Eqn. S2). (c) Species associated spectra. Species A represents the initially prepared singlet excited state ($S_2$), which internally converts (IC) to a hot/unrelaxed $^1S_1$ (species B). The lifetime of state A is close to the temporal resolution of the instrument, and so its spectrum is not fully deconvolved (represented as a dashed spectrum). This state then structurally relaxes to form the cooled $S_1$ state C. The terminal species D is the triplet state seen in the nsTA, which appears at times longer than the time scale of this experiment, so the spectrum of D is omitted.
Figure S30. (a) Multiple wavelength fits and time constants from fsTA for the reference compound Bn-DAPP$^{2+}$ excited at 330 nm. (b) Population curves fit to an A → B → C–D sequential decay model (Eqn. S2). (c) Species associated spectra. Species A represents the initially prepared singlet excited state (S$_n$), which internally converts (IC) to a hot/unrelaxed *S$_1$ (species B). The lifetime of state A is close to the temporal resolution of the instrument, and so its spectrum is not fully deconvolved (represented as a dashed spectrum). This state then structurally relaxes to form the cooled S$_1$ state C. The terminal species D is the triplet state seen in the nsTA, which appears at times longer than the time scale of this experiment, so the spectrum of D is omitted. Our model was chosen for simplicity, so some of the IC/relaxation dynamics may remain convolved.

Figure S31. (a) Multiple wavelength fits and time constants from nsTA for the reference compound Bn-DAPP$^{2+}$ excited at 505 nm. (b) Population curves fit to an A → B → GS (ground state) sequential decay model (Eqn. S5). (c) Species associated spectra. Species A represents the initially prepared singlet excited state, while species B is the triplet state.
Figure S32. (a) Multiple wavelength fits and time constants from nsTA for the reference compound Bn-DAPP$^{2+}$ excited at 414 nm. (b) Population curves fit to an A $\rightarrow$ B $\rightarrow$ GS (ground state) sequential decay model (Eqn. S5). (c) Species associated spectra. Species A represents the initially prepared singlet excited state, while species B is the triplet state.

Figure S33. (a) Multiple wavelength fits and time constants from nsTA for the reference compound Bn-DAPP$^{2+}$ excited at 330 nm. (b) Population curves fit to an A $\rightarrow$ B $\rightarrow$ GS (ground state) sequential decay model (Eqn. S5). (c) Species associated spectra. Species A represents the initially prepared singlet excited state, while species B is the triplet state.
Figure S34. (a) Multiple wavelength fits and time constants from fsTA for the reference compound Bn-ExBIPY²⁺ excited at 330nm. (b) Population curves fit to an A → B → C sequential decay model (Eqn. S3). (c) Species associated spectra. Species A represents the initially prepared singlet excited state, species B is the ion pair from forward electron transfer ($\tau_{FeT}$), and species C is the recombination to the triplet state after back electron transfer ($\tau_{BeT}$).

Figure S35. (a) Multiple wavelength fits and time constants from fsTA for DAPPBox⁴⁺ excited at 505 nm. (b) Population curves fit to an A → B → C sequential decay model (Eqn. S1). (c) Species associated spectra. Species A represents the initially prepared singlet excited state (*S₁), while species B is the structurally relaxed singlet excited state (S₁). The terminal species C is the triplet state seen in the nsTA, which appears at times longer than the time scale of this experiment.
Figure S36. (a) Multiple wavelength fits and time constants from fsTA for DAPPBox$^{4+}$ excited at 414 nm. (b) Population curves fit to an A $\rightarrow$ B $\rightarrow$ C$\rightarrow$ D sequential decay model (Eqn. S2). (c) Species associated spectra. Species A represents the initially prepared singlet excited state (S2), which internally converts (IC) to a hot/unrelaxed *S1 (species B). The lifetime of state A is close to the temporal resolution of the instrument, and so its spectrum is not fully deconvolved (represented as a dashed spectrum). This state then structurally relaxes to form the cooled S1 state C. The terminal species D is the triplet state seen in the nsTA, which appears at times longer than the time scale of this experiment, so the spectrum of D is omitted.

Figure S37. (a) Multiple wavelength fits and time components from fsTA for DAPPBox$^{4+}$ excited at 330 nm. (b) Population curves fit to the model given in Eqn. S4. (c) Species associated spectra. The kinetic model shows $^1$ExBIPY$^{2+}$ (species 1A) energy transferring to $^1$DAPP$^{2+}$ (1B) in 0.3 ps, which then decays in 20 ns (fixed time constant in the fits). The model also incorporates a parallel process where $^1$DAPP$^{2+}$ (species 2A) undergoes forward electron transfer ($\tau_{FeT}$) to DAPP$^{3+}$– ExBIPY$^{**}$ in 1.5 ps (species 2B). This state then structurally relaxes in 106 ps, as observed in the Figure S10, to form species 2C before undergoing back electron transfer ($\tau_{BeT}$) in 3.2 ns.
Figure S38. (a) Multiple wavelength fits and time constants from nsTA for DAPPBox$^{4+}$ excited at 505 nm. (b) Population curves fit to an A → B → GS (ground state) sequential decay model (Eqn. S5). (c) Species associated spectra. Species A represents the initially prepared localized singlet excited state, $1^*\text{DAPP}^2^+$, while species B is the triplet state.

Figure S39. (a) Multiple wavelength fits and time constants from nsTA for DAPPBox$^{4+}$ excited at 414 nm. (b) Population curves fit to an A → B → GS (ground state) sequential decay model (Eqn. S5). (c) Species associated spectra. Species A represents the initially prepared localized singlet excited state, $1^*\text{DAPP}^2^+$, while species B is the triplet state.
Figure S40. (a) Multiple wavelength fits and time constants from nsTA for DAPPBox⁴⁺ excited at 330 nm. (b) Population curves fit to an A → B → GS (ground state) sequential decay model, and a parallel C → GS model (1:1: initial population; Eqn. S6). (c) Species associated spectra. Species A represents the initially prepared singlet state, which decays with τ₅₁ to the triplet state B. This state decays to the ground state with τ₆. Forward electron transfer occurs before the time window, meaning species C represents the ion pair state (DAPP³⁺•–ExBIPY•⁺) and decays by back electron transfer (τ_BET).

8. Quantum Mechanical Calculations

Time-dependent density functional theory (TD-DFT) was employed for excited-state modeling, and the B3LYP/6-31G** level of approximation was used as the underlying kernel, with the asymptotic correction.¹⁰ The solvent effect of MeCN was accounted for with the SMD model.¹¹ All calculations were performed using the NWChem.¹² Predicted excitation of DAPPBox⁴⁺, at 338 nm, projected onto molecular orbital contributions, is shown in Figure S41, while Table 1 and Table 2 summarizes the stimulation of singlet and triplet excitations of DAPPBox⁴⁺ respectively.
Figure S41. Molecular orbital simulation of DAPPBox$^{4+}$ excited at 338 nm.

Figure S42. Electron density difference contours of the 1$^{\text{st}}$ (left) and 2$^{\text{nd}}$ (right) ion-pair excited states, with excitation energies of 2.47 and 3.74 eV, respectively. The red and blue colors represent extra electron hole density, respectively.

Table 1. Simulation of Singlet Excitations of DAPPBox$^{4+}$

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<tr>
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Table 2. Simulation of Triplet Excitations of DAPPBox$^{4+}$

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<tr>
<td>Intensity</td>
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Singlet-triplet transitions are forbidden without spin-orbit coupling (SOC), so intensities of triplet excitations cannot be determined.
9. References


(7) The MathWorks, Inc., Natick, Massachusetts, United States.


