Noncovalent Interactions

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The Chameleonic Nature of Diazaperopyrenium Recognition Processes**

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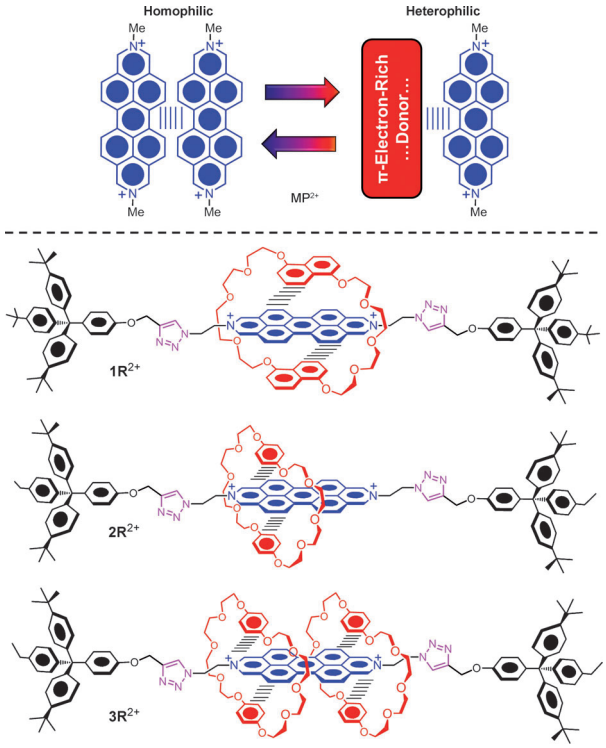
Two broad classes (Scheme 1) of molecular recognition processes[1] can be defined[2]—namely, 1) homophilic recognition, which involves the interaction of structurally and electronically similar, if not identical, species, and 2) heterophilic recognition in which constitutionally different species come together as a result of stabilizing intermolecular noncovalent bonding interactions. Nowhere are these concepts more relevant than when considering donor–acceptor recognition processes[3] between π-electron-rich and π-electron-deficient species. These donor–acceptor recognition motifs have aided and abetted the template-directed synthesis[4] of mechanically interlocked molecules[5] (MIMs), which have been employed in molecular electronic devices[6] (MEDs) and integrated bulk systems,[7] as well as in current state-of-the-art solar-cell technologies.[8]

Many of these donor and acceptor units are also capable[9] of undergoing reversible one-electron redox processes, leading to stable radical intermediates which engage[10] in homophilic radical–radical interactions as a result of dimerization—often referred to as pimerization[11] in the older literature. Recently, we have demonstrated[12] that these homophilic radical–radical interactions can be exploited in the template-directed synthesis[4] of MIMs, while other researchers have shown[13] that they can be used to fabricate organic solid-state semiconducting materials. There are very few examples of π-electronic organic molecules, however, which can exhibit both hetero- and homophilic recognition in a single redox state. This exceptional behavior, wherein the molecule can exhibit both recognition processes, analogous to that of a chameleon within its environment, is chameleonic in nature. These rare molecules have the potential to be incorporated into nanoscale architectures and functional building blocks for MIMs,[5] MEDs,[6] and other integrated devices.[7,8] Herein, we report 1) the solid-state superstructure of the dimethyldiazaperopyrenium dication[14] (MP^{2+}) based



Scheme 1. The chameleonic nature of MP^{2+} allows for homophilic molecular recognition even as a dicationic species, as well as donor–acceptor interactions with π-electron-rich compounds. These provide an example of heterophilic recognition, which has been harnessed in the template-directed synthesis of the [2]rotaxanes $\mathbf{1R}^{2+}$ and $\mathbf{2R}^{2+}$ in addition to the [3]rotaxane $\mathbf{3R}^{2+}$.

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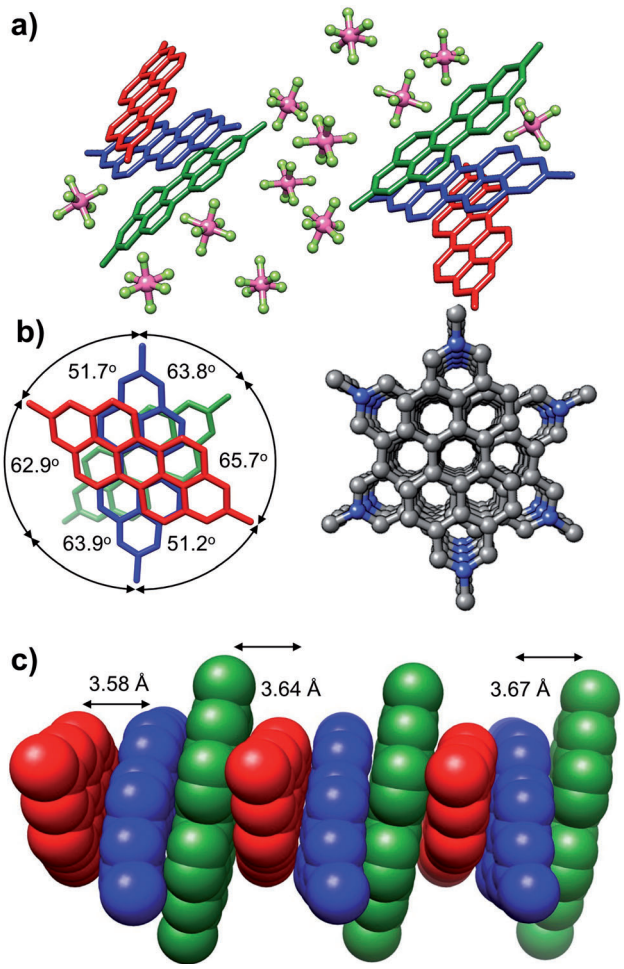


Figure 1. Solid-state (super)structures of MP·2 PF_6 illustrated by the a) colored framework of MP^{2+} and ball-and-stick representation of the 12 PF_6^- ions in one crystallographically independent cell with b) rotational stacking arrangement of the unit cell's three crystallographically independent MP^{2+} dications (red, blue, and green), and c) the space-filling representation of the continuous π stack of MP^{2+} ions. The distances between the central C–C bonds are approximately 3.6 Å, consistent with van der Waals interactions.

on the X-ray diffraction analysis[15] of single crystals whose 2) needlelike morphology is maintained on a SiO_2 surface, as revealed by scanning electron microscopy (SEM), and whose 3) potential electronic properties were assessed by quantum mechanical calculations based on density functional theory (DFT). These homophilic characteristics of the MP^{2+} dication are accompanied by 4) their ability to serve equally well in a heterophilic capacity as π-accepting guests in their complexation with π-donating aromatic crown ether hosts, thus making it possible 5) to template the syntheses of [3]- and [2]rotaxanes by using the supramolecular assistance[16] provided by π–π stacking and other noncovalent bonding interactions.

Orange needlelike single crystals, suitable for X-ray structural analysis,[15] were grown by slow vapor diffusion of iPr_2O into a solution of MP·2 PF_6 in MeCN. The unit cell contains six MP^{2+} dications and 12 PF_6^- counterions, thus confirming the dicationic nature of the organic component in the solid state. These six dications in the unit cell consist (Figure 1a) of two columns of three crystallographically independent MP^{2+} dications, separated by the 12 counterions and stacked one on top of the other at van der Waals distances: the two stacks are related by a crystallographic center of inversion. A closer inspection (Figure 1b) of the trio of repeating dications in the stacks reveals that, rather than their forming an in-register stack in the solid state which would maximize the degree of π-overlap of the perylene cores, albeit at significant cost to Coulombic repulsions between the pyridinium peripheries, each MP^{2+} dication is rotated by approximately 60°—the "dihedral" angles between consecutive N^+–N^+ vectors range from 57.2° to 65.7°—with respect to its nearest neighbors.[17] It would appear (Figure 1c) that this packing arrangement maximizes π–π interactions[18]—with centroid to centroid separations of 3.58, 3.64, and 3.67 Å—and minimizes Coulombic repulsions. The net result is that the entire perylene core of the MP^{2+} dication experiences overlap from its neighbors, top and bottom, with the central six-membered aromatic rings forming a continuous repeating unit while the pyridinium subunits are devoid of any face-to-face π–π stacking interactions. Although this kind of

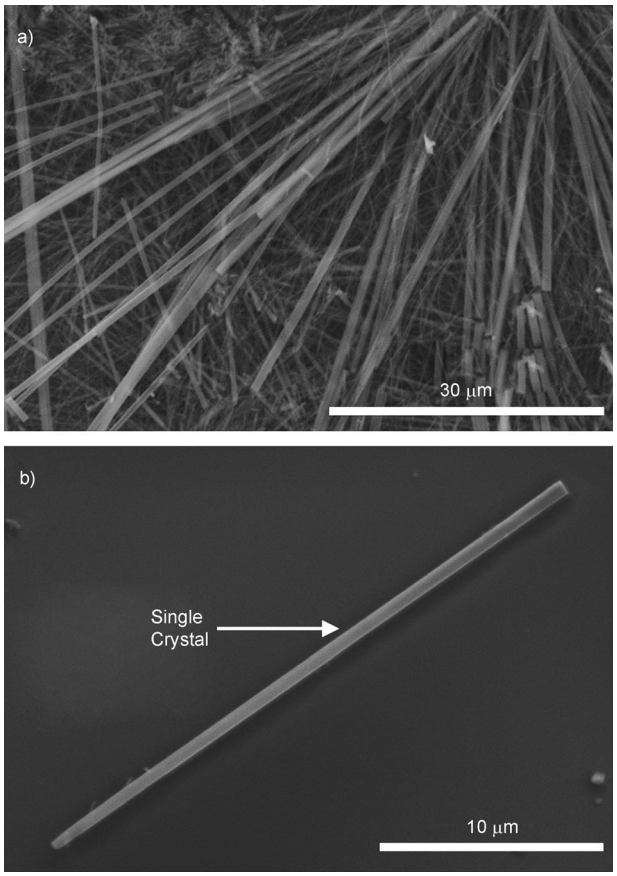


Figure 2. SEM measurements performed on crystals of MP·2 PF_6 grown directly on a SiO_2 surface from MeCN using slow vapor diffusion of iPr_2O at mother liquor concentrations of a) 1.2 mM, and b) 0.3 mM. At higher concentrations, thick bundles of fibers are observered, in agreement with X-ray crystallographic analysis. At lower concentrations—namely 0.3 mM—the molecules self-assemble to form single nanorods, which extend as long as 0.1 mm.

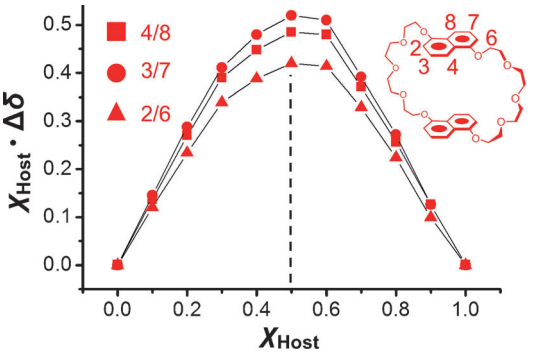


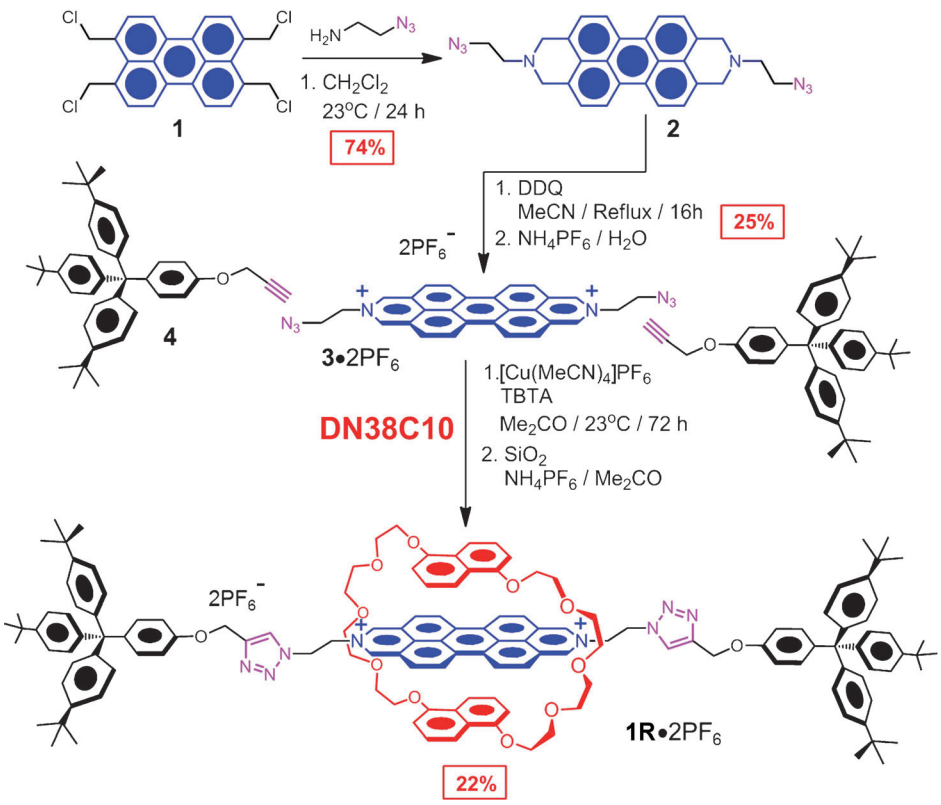
Figure 3. A Job plot between the DN38C10 host and the MP^{2+} guest obtained by plotting the $\Delta\delta$ value of the protons ($H_{2/6}$, $H_{3/7}$, $H_{4/8}$) of the DN38C10 ring observed by ^{1}H NMR spectroscopy (CD_3CN, 1.0 mM, 500 MHz, 298 K) against the change in the mole fraction (χ_{Host}) of the host. The plot indicates a 1:1 binding between the host and guest.

π–π stacking is relatively common for radical cations, such as the one ($MV^{\bullet+}$) obtained on reduction of methylviologen (MV^{2+}), it is rare for dications, for example, MV^{2+}, to exhibit a face-to-face homophilic stacking geometry. In the case of $MP{\cdot}2PF_6$, its packing in the solid state is reflected in its morphology on a substrate such as silica, where we have found it possible, at concentrations of about 0.3 mM, to grow single crystals that display needlelike morphologies on the surface of the silica, as indicated (Figure 2) by SEM.

The high-yielding synthesis (see Experimental Section and Supporting Information) of the $MP{\cdot}2PF_6$ affords us the opportunity to employ the molecular recognition of the MP^{2+} dication to template the synthesis of MIMs. Although we have reason[12,14] to believe that this objective could be achieved through the homophilic recognition expressed by the MP^{2+} dication, we have chosen to investigate the heterophilic recognition this dication displays towards π-electron-rich macrocyclic polyethers,[19] for example, bisparaphenylene[34]crown-10 (BPP34C10) and 1,5-dinaphtho[38]crown-10 (DN38C10). At the outset, we sought to obtain binding constants for the formation of the $MP^{2+}\subset$DN38C10 inclusion complex by carrying out a series of isothermal titration calorimetry (ITC) experiments, having already established the existence of a 1:1 complex from a Job Plot (Figure 3) on the basis of ^{1}H NMR spectroscopic measurements.[20]

All ITC measurements were performed (see the Supporting Information) in dry, degassed MeCN at 298 K. Experiments were repeated three times, and the thermodynamic parameters reported are the calculated averages of the three runs. The results confirmed a 1:1 binding event and revealed a binding constant K_a of $1.05\times10^4\,M^{-1}$, which corresponds to a free energy change (ΔG) upon binding of -5.48 kcal mol^{-1}. This K_a value for the $MP^{2+}\subset$DN38C10 complex, which is over an order of magnitude higher than that for $MV^{2+}\subset$DN38C10, is driven by a favorable change in enthalpy (ΔH) of -8.60 kcal mol^{-1}, which is mediated by a negative change in entropy (ΔS) of -10.5 cal mol^{-1} K^{-1}.

We have exploited the relatively large binding constant between MP^{2+} and DN38C10 to template the syntheses of rotaxanes (Scheme 2) with both DN38C10 and BPP34C10 by employing copper-assisted azide-alkyne cycloaddition[21–23] (CuAAC) to produce (see Experimental Section and the Supporting Information) the [2]rotaxanes $\mathbf{1R}^{2+}$ and $\mathbf{2R}^{2+}$, as well as a [3]rotaxane $\mathbf{3R}^{2+}$ in line with the reported[19] presence of the 1:2 complex, $MP^{2+}\subset(BPP34C10)_2$ in MeCN solution. The threading of two BPP34C10 onto a single MP^{2+} recognition site in $\mathbf{7}^{2+}$ offers a rare example of a rotaxane



Scheme 2. A facile synthesis of a diazaperopyrenium derivative employed in the preparation of the [2]rotaxane $\mathbf{5}{\cdot}2PF_6$. The tetrachloride **1** was converted using 2-azidoethanamine into the diazide **2** which was aromatized with DDQ to give the diazidoperopyrenium salt $\mathbf{3}{\cdot}2PF_6$, following counterion exchange. Complexation of DN38C10 with $\mathbf{3}^{2+}$ was followed by copper-catalyzed [3+2] cycloadditions to stopper the complex with propargyl ether **4** of a substituted tetraarylmethane derivative, affording $\mathbf{1R}{\cdot}2PF_6$ in 22%, in addition to the dumbbell in 24%.

where two donor rings share one acceptor unit in the dumbbell.

The chameleonic nature of the diazaperopyrenium dication is evident from 1) its propensity, on the one hand, to aggregate with itself in solution from whence, under the appropriate conditions, it crystallizes as an extended helical-like π–π stack and 2) its ability, on the other hand, to form stable complexes with π-electron-rich aromatic crown ethers in acetonitrile solution from which it is possible to obtain rotaxanes by heterophilic templation[12] under kinetic control.

Experimental Section

MP·2 PF_6: 1,3,8,10-Tetrahydro-2,9-dimethyl-2,9-diazadibenzo[*cd,lm*]-perylene[24] (100 mg, 274 mmol) was suspended at 23 °C in anhydrous MeCN (10 mL). 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; 249 mg, 1.10 mmol) was added as a solid, thereby resulting in an immediate color change from green to dark brown. The reaction mixture was heated under reflux for 16 h, before being cooled to 25 °C. A solution of 37% HCl (3 mL) was pipetted into the flask, whereupon precipitation occurred. The precipitate was filtered off and washed with MeCN (3 × 25 mL) and Et_2O (3 × 25 mL) to afford the dark green MP·2Cl (100 mg). Counterion exchange was performed by dissolving the dichloride salt in MeOH/H_2O (1:1) mixture, adding an excess of NH_4PF_6, and evaporating off the MeOH. The resulting precipitate was filtered and washed with an excess of H_2O to afford MP·2 PF_6 (136 mg, 77%). ^{1}H NMR (500 MHz, $(CD_3)_2CO$, 25 °C): $\delta = 10.21$ (s, 4H), 9.99 (d, $J = 9$ Hz, 4H), 9.00 (d, $J = 9$ Hz, 4H), 5.11 ppm (s, 6H; see Figure S1 in the Supporting Information). ^{13}C NMR (125 MHz, CD_3CN, 25 °C): $\delta = 139.1$, 128.6, 128.3, 127.8, 126.0, 121.4, 49.0 ppm. HRMS (ESI) calcd for $C_{26}H_{18}F_6N_2P$: $m/z =$ 503.1106 $[M]^+$, found: $m/z = 503.1106$ $[M]^+$ (see Figure S2 in the Supporting Information).

2: The tetrachloride[25] **1** (130 mg, 58.1 mmol) was added to 2-azidoethanamine (4.99 g, 290 mmol) dissolved in CH_2Cl_2 (20 mL) and the reaction mixture was stirred at 23 °C for 48 h. The solvent was removed by evaporation under reduced pressure and the residue was suspended in H_2O, filtered, and washed with H_2O (2 × 50 mL) and Et_2O (2 × 50 mL) to afford a pure sample of the diazide **2** (102 mg, 74%) as a reddish-brown powder. ^{1}H NMR (500 MHz, CD_3SOCD_3, 23 °C): $\delta = 8.14$ (d, $J = 7$ Hz, 4H), 7.23 (d, $J = 7$ Hz, 4H), 3.91 (s, 8H), 3.56 (t, $J = 6$ Hz, 4H), 2.80 ppm (t, $J = 6$ Hz, 4H). ESI-MS calcd $m/z =$ 472.2 $[M]^+$, found $m/z = 472.1$ $[M]^+$.

3·2 PF_6: The diazide **2** (101 mg, 0.213 mmol) was suspended in anhydrous MeCN (25 mL) at 23 °C, DDQ (388 mg, 1.71 mmol) was added, and the reaction mixture was heated under reflux for 16 h before being cooled to 23 °C. A solution of 37% HCl (3 mL) was pipetted into the mixture, whereupon precipitation occurred. The precipitate was filtered and washed with MeCN (3 × 25 mL) and Et_2O (3 × 25 mL) to afford (66 mg, 57%) the dark red dichloride salt of **3**·2Cl. Counterion exchange was performed by dissolving the salt in Me_2CO/H_2O (1:1), adding excess of NH_4PF_6, and evaporating off the Me_2CO. The resulting precipitate was filtered and washed with excess of H_2O to afford the crude product. Recrystallization from Me_2CO and Et_2O afforded (44 mg, 25% yield) **3**·2 PF_6. ^{1}H NMR (500 MHz, $(CD_3)_2CO$, 25 °C): $\delta = 10.43$ (s, 4H), 10.21 (d, $J = 9$ Hz, 4H), 9.17 (d, $J = 9$ Hz, 4H), 5.60 (t, $J = 5$ Hz, 4H), 4.58 ppm (t, $J = 5$ Hz, 4H) (see Figure S3 in the Supporting Information). ^{13}C NMR (125 MHz, CD_3CN, 25 °C): $\delta = 139.0$, 128.1, 126.4, 61.5, 53.6 ppm. HRMS (ESI) calcd for $C_{28}H_{20}F_6N_8P$: $m/z = 613.1453$ $[M]^+$, found: $m/z = 613.1447$ $[M]^+$.

1R·2 PF_6: The stopper precursor **4** (58 mg, 0.012 mmol) and DN38C10 (37 mg, 0.058 mmol) were added to a degassed solution of the diazide **3**·2 PF_6 (44 mg, 0.058 mmol) in Me_2CO/CH_2Cl_2 (40 mL, 3:1). The reaction mixture was stirred for 3 h at 23 °C before a catalytic amount of $[Cu(MeCN)_4]PF_6$ and tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine (TBTA) was added. The reaction mixture was stirred for an additional 3 days at 23 °C. After evaporation of the solvents, the crude product was subjected to column chromatography (SiO_2, CH_2Cl_2/MeOH (9:1) then 1% NH_4PF_6 in Me_2CO) followed by size-exclusion chromatography on Biobeads SX-1 with CH_2Cl_2 as the eluent. 1R·2 PF_6 was isolated as an orange solid (32 mg, 22%). ^{1}H NMR (500 MHz, CD_3CN, 25 °C): $\delta = 9.50$ (d, 4H, $J = 9$ Hz), 9.32 (s, 4H), 8.50 (d, 4H, $J = 9$ Hz), 8.07 (s, 2H), 7.12 (d, 12H, $J = 7$ Hz), 7.01 (d, 4H, $J = 7$ Hz), 6.97 (d, 12H, $J = 7$ Hz), 6.81 (d, 4H, $J = 7$ Hz), 5.99 (d, 4H, $J = 8$ Hz), 5.57 (t, 4H, $J = 5$ Hz), 5.31 (t, 4H, $J = 5$ Hz), 5.22 (t, 4H, $J = 8$ Hz), 5.04 (s, 4H), 4.97 (d, 4H, $J = 8$ Hz), 4.02 (m, 8H), 3.93 (m, 8H), 3.68 (m, 8H), 3.47 (m, 8H), 1.14 ppm (s, 54H; see Figure S4 in the Supporting Information). ^{13}C NMR (126 MHz, $(CD_3)_2CO$, 25 °C): $\delta = 157.5$, 152.9, 152.2, 149.2, 145.4, 145.2, 140.8, 138.6, 132.9, 131.4, 130.9, 130.0, 129.3, 128.9, 126.2, 125.8, 125.1, 124.2, 123.9, 114.7, 114.3, 112.7, 103.7, 72.4, 70.7, 68.5, 63.9, 63.0, 62.2, 51.6, 50.8, 34.8, 31.7 ppm. MS (MALDI) calcd for $C_{144}H_{158}F_6N_8O_{12}P$: $m/z =$ 2334.148, found: $m/z = 2334.015$ ($[M-PF_6]^+$), HR-MS (ESI) calcd for $C_{144}H_{158}N_8O_{12}$ $m/z = 1095.0933$, $m/z = 1095.0954$ ($[M-2PF_6]^{2+}$).

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[2] Here, we use the term homophilic recognition for specific examples that involve molecular recognition between like components, e.g., hydrogen bonding in supramolecular capsules and polymers or radical–radical interactions in π-organic radicals, as well as face-to-face π–π stacking in perylene diimides, while the term heterophilic recognition is used for some specific examples that involve molecular recognition between unlike components, e.g., crown ether/ammonium ion or donor–acceptor interactions.

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[15] Crystal data for $MP{\cdot}2PF_6$: $(C_{26}H_{18}N_2){\cdot}2(PF_6)$; orange tablet, $0.25\times0.03\times0.02\ mm^3$; triclinic, space group $P\bar{1}$; $a=10.7897(6)$, $b=14.9752(8)$, $c=24.7218(14)$ Å; $\alpha=91.131(4)$, $\beta=92.422(4)$, $\gamma=104.026(4)°$; $V=3870.1(4)$ Å^3; $Z=6$; $\rho_{calcd}=1.669\ g\,cm^{-3}$; $2\theta_{max}=57.9°$; $T=100(2)$ K; 10963 reflections collected; $\mu=2.547\ mm^{-1}$; $R1=0.0890$ [$I>2.0\sigma(I)$], $wR2=0.2754$ (all data).

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[18] The electrostatic potential map (see the Supporting Information) obtained from DFT calculations performed on a single MP^{2+} dication confirms that its most electron-deficient regions are indeed located around the tips of the pyridinium rings. Considering the facts that 1) the MP^{2+} dication is π-electron poor and 2) that its packing in the solid state is that of a continuous π – π overlapping array, we are led to speculate that single crystals of $MP{\cdot}2PF_6$ might exhibit semiconductivity. Indeed, the calculated HOMO – LUMO gap (2.8 eV) using B3LYP/6-31 + G**//B3LYP/6-31 + + G** is similar to the HOMO – LUMO gap (2.5 eV) for *N*,*N*′-dimethylperylene diimide, both of which were calculated by using the same DFT method—a compound known (M. Wewer, F. Stienkemeier, *Phys. Chem. Chem. Phys.* **2005**, *7*, 1171 – 1175) for its semiconducting behavior.

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[20] The inclusion complex of $MP^{2+}\subset$DN38C10 was investigated by UV/Vis spectroscopy. The expected charge-transfer band was not observed on account of the high extinction coefficient associated with the π–π* transitions in the MP^{2+} dication. Fluorescence spectroscopy performed on the same complex, however, provided some valuable insight into the charge-transfer interaction as a result of fluorescence quenching (see the Supporting Information). During the titration of DN38C10 into a solution of $MP{\cdot}2PF_6$, a signifigant decrease in the MP^{2+} fluorescence intensity was observed. Fluorescence quenching is postulated to occur by a one-electron transfer from the naphthalene subunit on the crown ether to the perylene core in the excited state.

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