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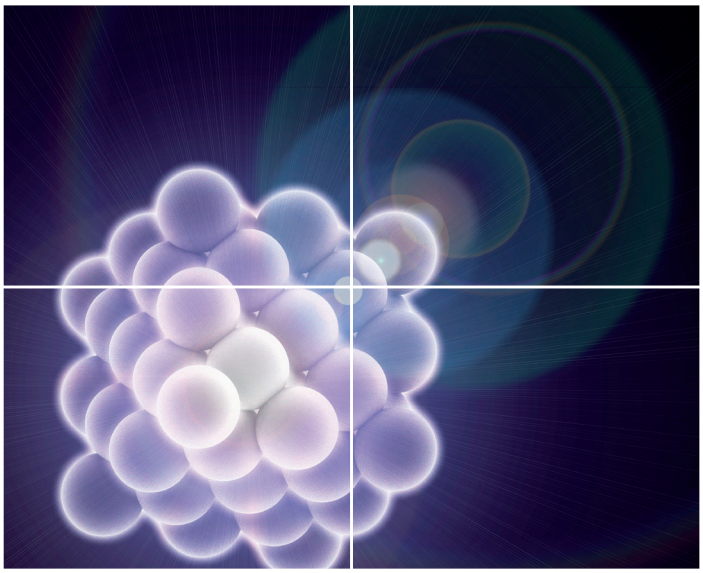

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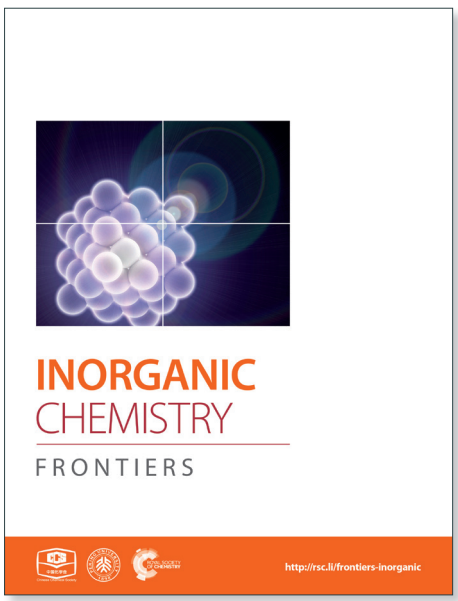

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ARTICLE TYPE

Synthesis of Naphthalenediimide-Based Cyclophane for Controlling Anion-Arene Interactions

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A cationic cyclophane based on a photoactive naphthalenediimide (NDI) moiety and on cationic triazolium units has been prepared. This system was employed to control the interactions between anions and the NDI motif for tuning the charge transfer properties of the NDI with different anions. High selectivity was observed that fluoride anion preferred to interact with NDI through SOMO-LUMO based electronic transition to form NDI radical anions in solution. This cyclophane can crystallize to form porous lattice which allowed for a gradual leaking of the PF_6^- anions with replacement by smaller size halides. Charge transfer complexes were formed upon replacing the non-nucleophilic hexafluorophosphate anion with halides in the molecular crystals.

Introduction

There are considerable interests in the control of the interactions between chromophors in supramolecular systems.[1,2] Anions play important chemical and biological roles, there are three main kinds of anion-arene interactions which can be used to tune the photophysical properties of the arenes.[3] Cyclophanes are a large class of host molecules known to recognize a variety of guests ranging from inorganic and organic cations and anions to neutral molecules.[4] Also in the recognition process all known modes of binding have been exploited, like hydrogen bonding, donor acceptor properties, cation-π interactions, and coordinate bonding.[4,5] However, using cyclophane to tune the anion-arene interactions for controlling the electron-transfer or charge-transfer process concerning anion guest is rare.

One way to accomplish such task is to combine proper photoactive moiety with known binding motifs into a single cyclophane.[4] In this capacity, naphthalenediimide (NDI)[6] was chosen because of its remarkable photochemical and electrochemical properties,[7-9] and the electron deficient and aromatic nature of NDI is important for anion-π interactions [3] for harness the charge-transfer properties. 1,2,3-Triazoles are new motifs that can participate in multiple noncovalent interactions.[10-13] Halides were chosen as the anion species because halides as the electrically charged donor units are known to form donor/acceptor complexes easily.[14] In this paper, we first present the preparation of a cationic cyclophane based on a photoactive NDI moiety and on cationic triazolium units by taking advantage of the ubiquitous Cu(I)-catalyzed "click chemistry".[15,16] Secondly, the anion-binding properties of this cationic macrocyclic host are employed to control the interactions between anions and the NDI motif for tuning the properties of the NDI.

Results and discussion

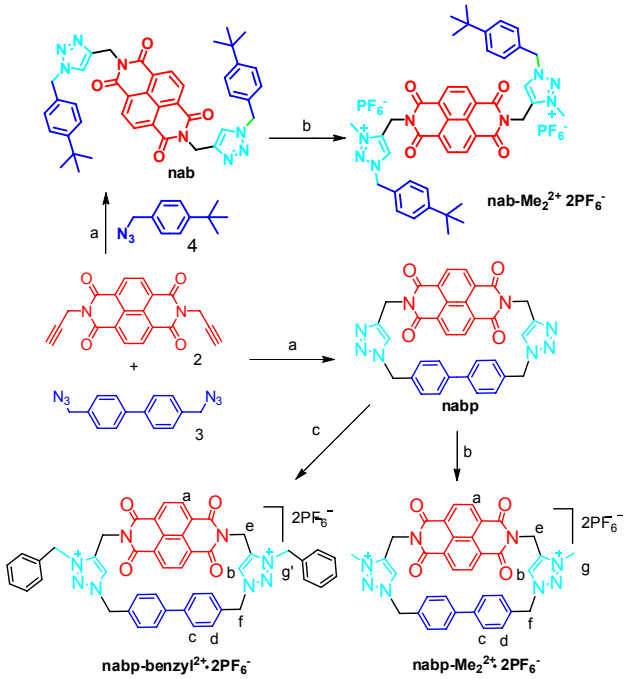
Synthesis and characterization of NDI cyclophane

The cationic macrocycle **nabp-Me$_2^{2+}$•2PF$_6^-$** (Scheme 1) was designed to provide such a structure wherein the two triazolium linkers connecting the NDI to the biphenylene were used as the anion binding motifs as well as the rotator. The rotation of triazolium along the cavity can influence the distance from the complexed anion to NDI, further tune the electron-transfer or charge-transfer process from the anions to NDI. **nabp** was methylated with MeI in DMF solution and ion-exchanged into its PF_6^- salt **nabp-Me$_2^{2+}$•2PF$_6^-$**. **nabp-Me$_2^{2+}$•2PF$_6^-$** showed good solubility in polar solvents like acetonitrile, acetone, DMF. **nabp-benzyl^{2+}•2PF$_6^-$** was synthesized in the similar way to enhance the solubility for titration study. **nab-Me$_2^{2+}$•2PF$_6^-$** was synthesized as the reference compound to investigate the role of cyclophane. **nabp**, **nabp-Me$_2^{2+}$•2PF$_6^-$** and **nabp-benzyl^{2+}•2PF$_6^-$** were fully characterized by ^{1}H NMR, ^{13}C NMR, MS spectra.

NMR spectra of **nabp** at room temperature indicate that the biphenylene moiety rotates rapidly on the NMR time scale (Figure S1). However, upon decreasing the temperature from 298 to 228 K the dynamic processes are slowed, resulting in separation of the signals and the coalescence temperature is at about 298 K. At the same time, the triazole proton H_b and the biphenylene proton H_d (close to triazole) shifted down-field with the decreasing of the temperature, which is consistent with the shielding effect between triazole and biphenyene groups when the movement of triazole and biphenylene groups were slowed.

X-ray diffraction analyses

The crystal and molecular structures of **nabp-Me$_2^{2+}$•2PF$_6^-$** were determined by X-ray diffraction analyses. **nabp-Me$_2^{2+}$•2PF$_6^-$**



Scheme 1. Reaction conditions: a) Dropwise addition of **2** and **3** into CuI / DBU / PhMe / Ar over 10 h, stir another 4 h, 70 °C, 50%. b) MeI, CH_2Cl_2/DMF, 40 °C, 24h; NH_4PF_6, acetone/H_2O, 85%. c) benzyl chloride, CH_2Cl_2/DMF, 40 °C, 48h; NH_4PF_6, acetone/H_2O, 73%.

crystallizes in a monoclinic system with a P2(1)/c space group with four molecules in a unit cell. (Table S1, Figure 1). X-ray crystal structure confirmed that N-methylation preferentially occurred at the N3 and N8, which is in agree with the reactivity of nitrogen in triazole.[17] The distance between two triazole hydrogens is 7.816 Å. Single-crystal X-ray analyses revealed that the diimide NDI and 4,4'-biphenylene residues in **nabp-Me$_2^{2+}$•2PF$_6^-$** are oriented face-to-face across the centre of the macrocycle (Figure 1 down). The transannular (centroid–centroid) separation is 6.336 Å (C13-C26), slightly longer than that at the terminal nitrogen imide positions with 5.635 Å (C30-N1). In the unit cell, triazolium plane π–π stacked with biphenylene group (Figure 1 down, red).

Packing diagram showed that **nabp-Me$_2^{2+}$•2PF$_6^-$** is also a cationic three-dimensional structure with infinite chains composed of alternating **nabp-Me$_2^{2+}$** box and PF_6^- anions (Figure 2). **nabp-Me$_2^{2+}$•2PF$_6^-$** contains channels that run along the length of *a* or *c* axes (Figure 2). In the direction of *a* axe, one kind of channel formed from the cavity of the cyclophane, in which CH_3CN molecules is inserted, with distances between the nitrogen of acetonitrile and the centroids of the biphenyl linkage and the imide ring system of 3.25 and 3.06 Å, respectively. The distance between nitrogen of acetonitrile and triazolium C-H of 2.536 Å was also observed. Another kind of channel formed between neighbour cyclophanes, which was driven by the electrostatic interaction between the cationic cyclophane framework and PF_6^- anions. In the X-ray crystal structure of **nabp-Me$_2^{2+}$•2PF$_6^-$**, there are ordered and heavily disordered PF_6^- anions and acetonitrile molecules, the disordered species oscillated in the channel, which supporting only weak electrostatic interaction between the cationic cyclophane and

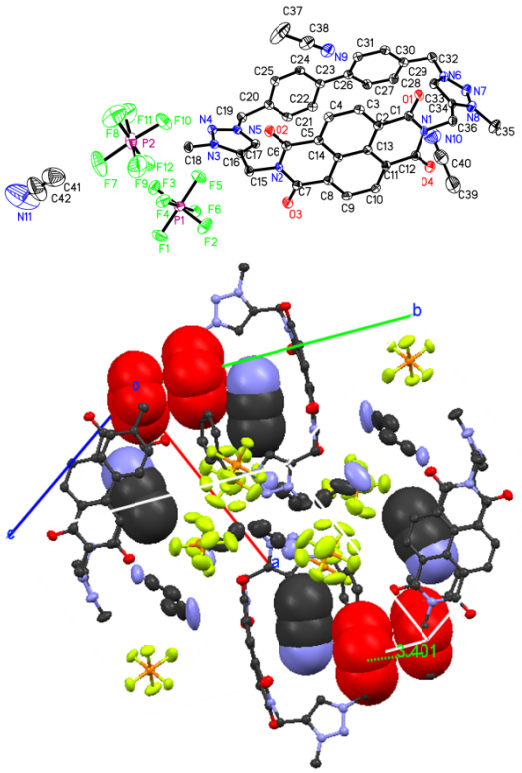


Figure 1. ORTEP diagram and atomic labeling of the cyclophane **nabp-Me$_2^{2+}$•2PF$_6^-$** (Thermal ellipsoids are shown at 50% probability) (top); Side view and top view of **nabp-Me$_2^{2+}$•2PF$_6^-$** in the unit cell (down), CH_3CN (space filling) reside in each cyclophane, π–π stacked triazolium and biphenylene are indicated (red, space filling). Torsion angle at the biphenyl linkage is 18–19º in the macrocycle.

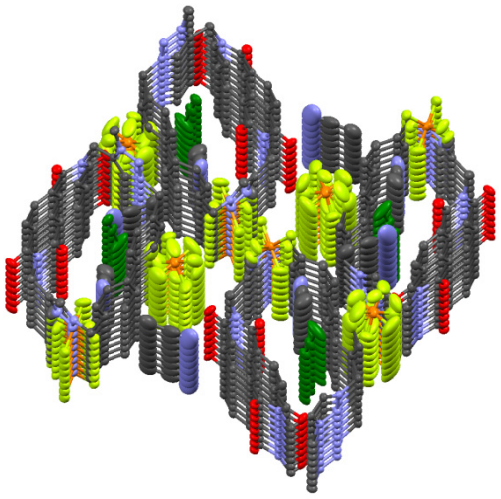


Figure 2. Channels formed by the **nabp-Me$_2^{2+}$•2PF$_6^-$** framework, running along the length of the *a*-axis (carbon: gray; phosphate: brown; fluoride: yellow; oxygen: red; nitrogen: blue; hydrogen was omitted for clarity).

charge-balancing PF_6^- anions. This weak electrostatic interaction and the porous nature of the lattice may allow for a gradual leaking of the PF_6^- anions with replacement by smaller size halides. These features are important for the anion exchange that will be discussed below.

Cyclic voltammetry studies

Cyclic voltammetry gave E_f^0 values of -0.932 and -1.425 V versus Fc^+/Fc for **nabp**, -0.82V, -1.26V, -2.132V and -2.242V versus Fc^+/Fc for **nabp-Me$_2^{2+}$•2PF$_6^-$** (Figure 3). The first electron reduction potential (*E*1) of NDI in **nabp-Me$_2^{2+}$•2PF$_6^-$** is 0.112 V larger than that in **nabp**. These results indicated that the electron acceptability of NDI is influenced greatly by the nearby triazolium moieties which electrostaticly stabilize the NDI anion. The methylation further lower the low-LUMO (LL) of NDI compounds, which will help the electron-transfer from anions to NDI to form the SOMO-LUMO based electronic transitions.[18]

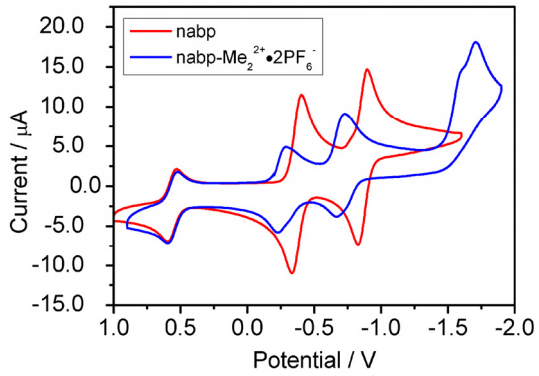


Figure 3: a) CV of **nabp** and **nabp-Me$_2^{2+}$•2PF$_6^-$** in DMF with ferrocene/ferricenium couple (Fc/Fc) as internal standard. (**nabp** and **nabp-Me$_2^{2+}$•2PF$_6^-$**, 0.1 mM; $TBAPF_6$ = 0.1 M).

Cyclophane-halide anion interactions in solution

The fluoride anion induces the formation of the radical anion of NDI which in turn displays various SOMO-LUMO electronic transitions. Upon the addition of fluoride, **nabp-Me$_2^{2+}$•2PF$_6^-$** showed an instantaneous change from colorless to dark brown. UV-vis-NIR spectroscopy of **nabp-Me$_2^{2+}$•2PF$_6^-$** show peaks at 358 and 377 nm. In the presence of fluoride, a new set of intense and characteristic visible and near-infrared (NIR) absorption bands for NDI radical anions at 476, 608, 701, 782 nm appeared (Figure 4a). These new peaks at 476–786 nm for **nabp-Me$_2^{2+}$•2PF$_6^-$** with fluoride and their relative intensity ratios perfectly match with the signature peaks due to D_0-D_n electron transfer for the radical anions of the NDI moiety.[18] The other strong evidence for the NDI radical anions comes from the diagnostic EPR signal unique to the imide radicals (*g*, 2.0056) of [**nabp-Me$_2^{2+}$**]•$^-$, formed in the presence of fluoride (Figure 4b).[19] The fluoride ion was oxidized as supported by the disappearance of ^{19}F NMR signal at 102 ppm upon the addition of one equivalent of **nabp-Me^{2+}•2PF$_6^-$** (Figure S13).[18b] UV-vis-NIR titration using other halides (Cl^-, Br^- and I^-) indicated that only F^- produces the NDI radical anion species (Figure S11). **nab-Me$_2^{2+}$•2PF$_6^-$** can also interact with F^- and exhibit electron transfer behavior in the solution state to form NDI radical anion, but the interaction is weaker than in the case of **nabp-Me$_2^{2+}$•2PF$_6^-$**, as indicated by the fact that one equivalent of F^- can interact with 80% of **nabp-Me$_2^{2+}$•2PF$_6^-$**, while 30 equivalents of F^- are needed to interact with 80% of **nab-Me$_2^{2+}$•2PF$_6^-$** (Figure S12).

For the cyclophane system studied here, there are three main binding sites for anions, that is, triazolium C-H for hydrogen bond, cationic triazolium ring for electrostatic interaction, electron-deficient NDI for anion-π interaction. Triazole-based C^5–H H-bonds are aided by the relatively large 5-Debye dipole,[20,21] with its positive end directed almost in line with C^5–H bond. The anion binding properties of **nabp-benzyl^{2+}•2PF$_6^-$** were investigated by titrating with tetrabutylammonium (TBA^+) halide salts of Cl^-, Br^- and I^- in CD_3CN (Figure S4-6). The triazolium proton H_b and the methene proton H_e linked to the imide shifted downfield upon addition of anions. The shift of the triazolium H_b could attribute to the hydrogen bonding interaction contributed by anions, proton H_e interact with the halides brought close by the triazolium. Furthermore, the remaining aromatic protons do not shift very much during the titration suggesting the primary role that the triazolium serve in binding the halide anion. The shift of proton H_b decreased with the increasing of the size of the halides. For methene proton H_e and biphenylene proton H_d, similar shift trends were observed though at smaller extent. On account of the shape flexibility of this cyclophane (VT ^{1}H NMR, Figure S1), there is an evident energy cost that is associated with a change in the conformation of the receptor,[22] the anion binding affinity of this cyclophane is limited. **nabp-benzyl^{2+}•2PF$_6^-$** showed binding constants of 125 M^{-1} for Cl^-, 63 for Br^-, 45 for I^- (from chemical shift of triazolium CH, Figure S6). **nabp-Me$_2^{2+}$•2PF$_6^-$** will precipitate with the addition of halides in normal solvents, thus the binding affinity were investigated in DMSO (Figure S7-9), **nabp-Me$_2^{2+}$•2PF$_6^-$** showed binding constants of 43.7 M^{-1} for Cl^-,

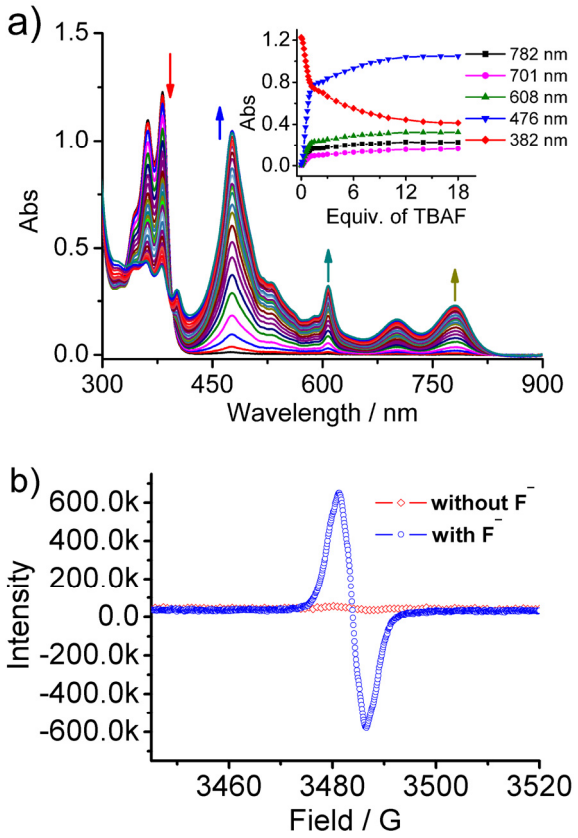


Figure 4. a) UV-vis-NIR spectra showing the response of **nabp-Me$_2^{2+}$•2PF$_6^-$** (5.0×10^{-5} M) upon incremental addition of F^-, **nabp-Me$_2^{2+}$•2PF$_6^-$** in DMF. Inset shows the response of the optical channels as a function of F^-. b) ESR spectra of **nabp-Me$_2^{2+}$•2PF$_6^-$** and **nabp-Me$_2^{2+}$•2PF$_6^-$** in presence of F^- in DMF (**nabp-Me$_2^{2+}$•2PF$_6^-$**, 1.0×10^{-4} M).

16.7 for Br^-, 8.5 for I^-. These results indicated that triazolium C–H···X^- decreased with the increasing of anion size, and triazolium C-H prefer to stretch out to bind with anions with the cooperation of H_e and biphenylene proton H_d. ^1H NMR titration of F^- showed the broadening of the spectra of the receptor (Figure S2) which could be explained by the formation of the NDI radical anions.

Cyclophane-halide anion interactions in the solid state

A charge transfer complex is expected to form upon replacing the non-nucleophilic hexafluorophosphate anion with halides in the presence of a cationic moiety incorporating a strong electron accepting naphthalene diimide moiety.[23] The rotation property of triazolium C–H···X^- and the larger size of Cl^-, Br^-, I^- prohibited the observation of evident charge transfer from halide to NDI in solution. Constraining the movements of the molecules, the anion-triazolium ion-pair can contact with NDI closely, charge transfer phenomena occurred. For example, by simply immersing as-synthesized **nabp-Me$_2^{2+}$•2PF$_6^-$** crystals in 0.1 M TBAF, TBACl, TBABr, TBAI solution at room temperature for 3 days, the colour of the crystals became different with each other, pale yellow for F^-, yellow for Cl^-, red-brown for Br^-, dark brown for I^- (Figure 5 A-E). FTIR and PXRD (Figure S 15, 16) indicated that the replacement of the larger PF_6^- anions with the smaller halides anions through a diffusion process occurs at the solid-liquid interface.[24] **nab-Me$_2^{2+}$•2PF$_6^-$** didn't show this behavor (Figure S17).

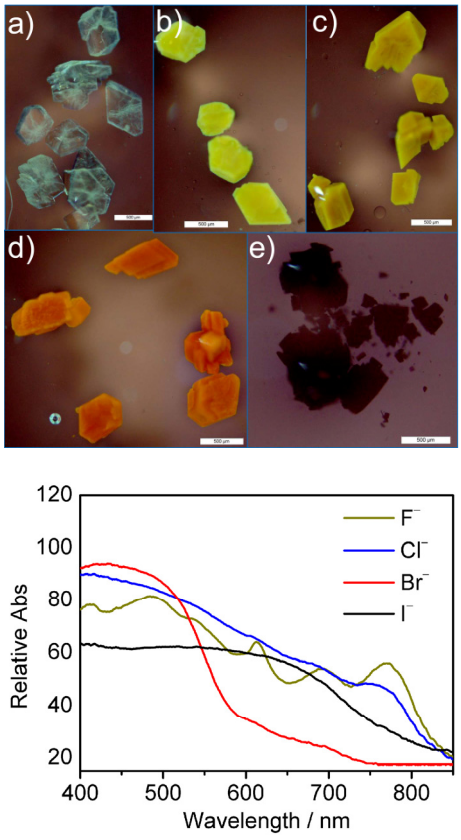


Figure 5. Optical micrographs of **nabp-Me$_2^{2+}$** crystals before (a) and after anion exchange with F^- (b), Cl^- (c), Br^- (d), I^- (e). (scale bar: 500 μm). Reflection UV-vis spectra (down) of the complexes of **nabp-Me$_2^{2+}$** with F^-, Cl^-, Br^- and I^- (in KBr pellet).

Reflection UV-vis spectra of the complexes for Br^- and I^- showed broad charge-transfer (CT) band at 400–580 nm, 400–750 nm, respectively (Figure 5 right). While for F^- and Cl^-, the color of the KBr pellet made by high pressure is different from the anion-exchanged solid and the powder, the characteristic peaks for the radical anions of the NDI were observed. That is, under high pressure, F^- and Cl^- can contact with NDI moiety closely for formation of NDI radical anions; charge-transfer complexes are preferred to be formed after replacing the non-nucleophilic hexafluorophosphate anion with halides in the molecular crystals.

Conclusions

In summary, a cationic cyclophane based on a photoactive NDI moiety and on cationic triazolium units has been prepared and was employed to control the interactions between anions and the NDI motif. The fluoride anion induces the formation of the radical anion of NDI which in turn displays various SOMO-LUMO electronic transitions. Charge-transfer complexes are preferred to be formed between NDI and Cl^-, Br^- or I^- with the constraining of the movement of the molecules in the solid state. Visible charge-transfer absorptions for the charge transfer complexes of the halides in the molecular crystals encourage their use in the design of functional molecular crystal and materials for studying photoinduced electron transfer and energy conversion for application in the field of molecular electronics.

Experimental section

General considerations

All reagents were obtained from commercial suppliers and used as received unless otherwise noted. Column chromatography was performed on silica gel (160–200 mesh), and thin-layer chromatography (TLC) was performed on precoated silica gel plates and observed under UV light. Nuclear magnetic resonance (NMR) spectra were recorded on Bruker Avance DPS-400 and Bruker Avance DPS-600 spectrometers at room temperature (298 K). Chemical shifts were referenced to the residual solvent peaks. Matrix-assisted laser desorption/ionization reflectron time-of-flight (MALDI-TOF) mass spectrometry were performed on a Bruker Biflex III mass spectrometer. Electronic absorption spectra were measured on a JASCO V-579 spectrophotometer. Fluorescence excitation and emission spectra were recorded using a Hitachi F-4500. The single crystal X-ray diffraction data were collected on a Rigaku Saturn X-ray diffractometer with graphite-monochromator Mo-Kα radiation (λ = 0.71073 Å) at 173 K. Intensities were corrected for absorption effects using the multi-scan technique SADABS (Siemens Area Detector Absorption Corrections). The structures were solved by direct methods and refined by a full matrix least squares technique based on F2 using SHELXL 97 program (Sheldrick, 1997). Compound **2** and **3** were synthesized in accordance with literature procedures.[25,26]

Synthesis of compound nabp

DBU (4.0 mmol, 0.7 mL) was added to toluene (200 mL), degassed (argon) for 30 minutes and heated to 70 °C while flushing with argon. At 70 °C, CuI (0.04 mmol, 6.6 mg) was

added to the mixture. A solution of the **2** (171 mg, 0.5 mmol) and **3** (132 mg, 0.5 mmol) in toluene (60 mL) was added to the solution slowly over 10 h and stirred for another 6 h under argon. The mixture was concentrated in vacuo. The product was purified via chromatography (SiO_2, $CHCl_3$: methanol 100: 3) to afford **nabp** (151 mg, 50% yield) as a pale yellow solid. ^{1}H NMR (400 MHz, d_6-DMSO) δ = 8.62 (s, 4 H), 7.58 (s, 2 H), 7.17 (d, 4 H, J = 8.2 Hz), 7.12 (d, 4 H, J = 8.2 Hz), 5.53 (s, 4 H), 5.33 (s, 4 H). MS (MALDI-TOF): m/z: calcd for $C_{34}H_{23}N_8O_4$ $[M+H]^+$: 607.2; found: 607.4. Elemental analysis calcd (%) for $C_{34}H_{22}N_8O_4$: C 67.32, H 3.66, N 18.47; found: C 67.26, H 3.71, N 18.39.

Synthesis of compound nabp-Me_2^{2+}•$(PF_6)_2^-$

Compound **nabp** (121 mg, 0.2 mmol) in 2 mL DMF and MeI (2 mL) was heated at 40 °C overnight, and the mixture was poured into 50 mL CH_2Cl_2 to obtain some precipitate, washed with CH_2Cl_2. The solid was suspended in acetone, NH_4PF_6 (5 equivalents) was added, the mixture became a clear solution, remove the solvent, washed the solid residue with water, dried under vacuo to obtain **nabp-Me_2^{2+}•$(PF_6)_2^-$** (165 mg, 85%). ^{1}H NMR (400 MHz, CD_3CN) δ = 8.65 (s, 4 H), 7.95 (s, 2 H), 7.35 (d, 4 H, J = 8.3 Hz), 7.25 (d, 4 H, J = 8.3 Hz), 5.67 (s, 4 H), 5.49 (s, 4 H), 4.40 (s, 6 H). ^{13}C NMR (100 MHz, CD_3CN, δ, ppm): 163.3, 141.9, 140.9, 133.1, 132.1, 130.6, 130.0, 128.0, 127.4, 127.3, 57.9, 39.4, 33.2. MS (MALDI-TOF): m/z: calcd for $C_{36}H_{28}N_8O_4$ $[M-2PF_6]^{2+}$: 636.2; found: 636.4. Elemental analysis calcd (%) for $C_{36}H_{28}F_{12}N_8O_4P_2$: C 46.66, H 3.05, N 12.09; found: C 46.71, H 3.02, N 12.04.

Synthesis of compound nabp-benzyl^{2+}•$(PF_6)_2^-$

Compound **nabp-benzyl^{2+}•$(PF_6)_2^-$** was obtained in the similar way as **nabp-Me_2^{2+}•$(PF_6)_2^-$**. (87 mg, 73%). ^{1}H NMR (400 MHz, CD_3CN) δ = 8.64 (s, 4 H), 7.83 (s, 2 H), 7.46 (m, 10 H), 7.39 (d, 4 H, J = 7.9 Hz), 7.29 (d, 4 H, J = 7.9 Hz), 5.97 (s, 4 H), 5.69 (s, 4 H), 5.48 (s, 4 H). ^{13}C NMR (100 MHz, CD_3CN) δ = 163.60, 141.92, 141.38, 132.97, 132.50, 131.31, 130.91, 130.77, 130.63, 130.43, 129.92, 128.48, 127.69, 58.62, 56.79, 33.85. MS (MALDI-TOF): m/z: calcd for $C_{48}H_{36}N_8O_4$ $[M-2PF_6]^{2+}$: 788.3; found: 788.4. Elemental analysis calcd (%) for $C_{48}H_{36}F_{12}N_8O_4P_2$: C 53.44, H 3.36, N 10.39; found: C 53.37, H 3.31, N 10.33.

Synthesis of compound nab

Compound **2** (171 mg, 0.5 mmol), **4** (190 mg, 1.0 mmol), DBU (4.0 mmol, 0.7 mL) was added to toluene (500 mL), degassed (argon) for 30 minutes and heated to 70 °C while flushing with argon. At 70 °C, CuI (0.04 mmol, 6.6 mg) was added to the mixture. Stirred for 12h under argon. The mixture was concentrated in vacuo. The product was purified via chromatography (SiO_2, $CHCl_3$: methanol 100: 3) to afford **nab** (270 mg, 75% yield) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 4 H), 7.59 (s, 2 H), 7.36 (d, J = 7.9 Hz, 4 H), 7.20 (d, J = 7.9 Hz, 4 H), 5.46 (d, J = 12.0 Hz, 8 H), 1.29 (s, 18 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.45, 151.91, 142.97, 131.38, 131.17, 127.98, 126.75, 126.59, 126.01, 123.19, 53.93, 35.56, 34.62, 31.23. MS (MALDI-TOF): m/z: calcd for $C_{42}H_{40}N_8O_4$ [M]+: 720.3; found: 720.4. Elemental analysis calcd (%) for $C_{42}H_{40}N_8O_4$: C, 69.98; H, 5.59; N, 15.55; found: C 69.94, H 5.53, N 15.48.

Synthesis of compound nab-Me_2^{2+}•$(PF_6)_2^-$

Compound **nab** (144 mg, 0.2 mmol) in 2 mL DMF and MeI (2 mL) was heated at 40 °C overnight. The mixture was concentrated in vacuo.washed with CH_2Cl_2. The solid was suspended in acetone, NH_4PF_6 (5 equivalents) was added, the mixture became a clear solution, remove the solvent, washed the solid residue with water, dried under vacuo to obtain **nab-Me_2^{2+}•$(PF_6)_2^-$** (165 mg, 80%). ^{1}H NMR (400 MHz, d_6-DMSO) δ 9.14 (s, 2 H), 8.74 (s, 4 H), 7.42 (q, J = 8.3 Hz, 8 H), 5.80 (s, 4 H), 5.49 (s, 4 H), 4.41 (s, 6 H), 1.24 (s, 18 H). ^{13}C NMR (100 MHz, DMSO) δ 163.15, 152.36, 139.60, 131.64, 131.14, 130.50, 129.23, 127.00, 126.76, 126.31, 56.17, 39.04, 34.86, 32.98, 31.40. MS (MALDI-TOF): m/z: calcd for $C_{44}H_{46}N_8O_4$ $[M-2PF_6]^{2+}$: 750.4; found: 750.5 Elemental analysis calcd (%) for $C_{44}H_{46}F_{12}N_8O_4P_2$: C 50.77, H 4.45, N 10.77; found: C 50.80, H 4.41, N 10.70.

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† Electronic Supplementary Information (ESI) available: Compound characterization data, NMR spectroscopy, NMR titrations isotherms, FTIR and PXRD spectra, and X-ray crystallofraphic data. See DOI: 10.1039/b000000x/

‡ *Crystallographic data* for **nabp-Me_2^{2+}•2PF_6^-**: $C_{42}H_{37}F_{12}N_{11}O_4P_2$,$M_r$ = 1049.77, monoclinic, space group = P2(1)/c, a = 13.697(2), b = 23.188(3), c = 14.177(2)Å, α = 90°, β = 95.173(2)°, γ = 90° T = 173 K, Z = 4, μ= 0.204 mm^{-1}, $R_F(R_{wF})$ = 0.0804 (0.1939) for 30215 observed independent reflections.

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