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Synthesis of a Naphthalene-diimide Cyclophane for Tuning Supramolecular Interactions by Metal Ions

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A new supramolecular species of naphthalene-diimide cyclophane containing triazole units was synthesized, and its fluorescent responses to metal ions were investigated in dichloromethane (DCM). The fluorescence emission of NDI was quenched by intramolecular electron transfer, whereas the appearance of dimer emission of the naphthalene-diimide in the presence of Mg^{2+}, Ba^{2+}, Hg^{2+}, Ca^{2+}, Zn^{2+} and Pb^{2+} was observed.

Introduction

Recently, great effort has been devoted to the design and synthesis of photo- and electroactive organic materials.[1] The design of novel organic molecules containing electron donors and acceptors constitutes a promising field because of the unique photoelectronic properties they can instill to donor–acceptor interactions. Efforts to understand electron transfer (ET) and/or charge transfer (CT) in these materials have attracted much attention over the past few decades[2] and have enabled the design of high-performance molecular materials. Such efforts have also led to the discovery of new applications of these systems, such as in molecular electronic devices,[3] nonlinear optical devices[4] and artificial photosynthetic systems.[5] A classic model system of intramolecular electron transfer is comprised of an electron donor (D) and an electron acceptor (A) connected by some molecular bridge (B).[6] The number and variety of such donor–bridge–acceptor (DBA) systems have grown explosively in recent years. Linkers for the D and A elements of these systems have been π-bond-conjugated bridges, [7] σ-bond bridges, and even hybrid-bond bridges.[8]

There has also been intense interest in the development of macrocycles by virtue of their high significance in areas as diverse as drug development[9] and supramolecular chemistry,[10] which can also be widely used for studies of catenanes, rotaxanes and transition-metal coordination chemistry.[11] 1,4,5,8-Naphthalenetetracarboxdiimide (NDI) derivatives possess an excellent π-conjugated system, low LUMO energy level and good molecular coplanar properties. These properties have proven useful for electronic exchange and transfer, and have been widely used in many fields, such as in solar cells,[12] photoconductors, electroluminescence, n-type organic semiconductors,[13] anion detection,[14] gas-storage materials,[15] molecular mechanical machines,[16] targeting specific DNA sequences[17] for purposes of cancer therapy and antibiotic development, and so on. Triazoles are new motifs that can participate in multiple noncovalent interactions such as metal coordination,[18] anion recognition[19] within flexible[20] and shape-persistent triazolophanes[21] and in foldamers,[22] and they can also assist in self-assembly.[23] An application of increasing importance is the use of triazoles as electron donors due to their ability to selectively form complexes, which can sharply change spectral properties. By using such molecules that combine different receptor units such as π-conjugated systems and crown ethers not only expands the functionality of the system, but also provides a means to control physical properties.

In this work, we have designed and synthesized a new symmetric, and highly rigid, molecule containing the cyclic NDI dyad, in which triazole donor and NDI acceptor are linked by short alkyl units. Besides serving as the electron donor, the triazole can function also as a potential binding site for metal ions. The tuning of the photoinduced electron transfer in this cyclophane was also performed with the help of metal ions. Divalent metal ions such as Mg^{2+}, Ba^{2+}, Hg^{2+}, Ca^{2+}, Zn^{2+} and Pb^{2+} can turn off the intramolecular electron transfer from triazole to NDI by coordinating with the carbonyl oxygen and triazole nitrogen moieties, followed by turning on the electron transfer between the NDI units, which leads to an enhanced dimer emission of the NDI.

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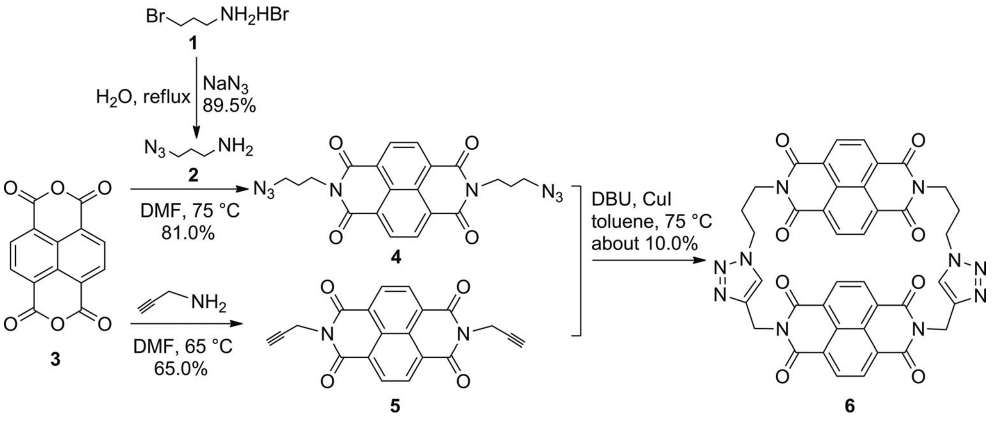
Results and Discussion

The synthesis of compound **6** from commercially available compounds is illustrated in Scheme 1. A solution of **1** dissolved in water containing 3 equiv. of sodium azide, which was refluxed overnight, afforded the desired amine **2**[24] in 89.5% yield as a colorless volatile oil. Compound **3** and 2.2 equiv. of **2** were combined and stirred in DMF at 75 °C overnight to yield diazide product **4**[25] as an analytically pure powder in 81.0% yield. Reaction of **3** with excess 2-propyn-1-amine under similar conditions afforded a 65.0% yield of dialkyne product **5**[26] in only 7 h. We envisioned the synthesis of **6** to be heavily influenced by concentration and to be favored by dilute conditions. Accordingly, a mixture of **4** and **5** in toluene was added dropwise to a stirred solution of CuI (0.1 equiv.) and DBU (0.05 equiv.) dissolved in a large volume of toluene under an inert gas at 75 °C over the course of 2 d. After another 3 d, TLC analysis indicated that the reaction was complete. It is noteworthy that cycloaddition between **6** and the DBU catalyst at high temperature was found to occur easily.[27] Furthermore, compound **6** was obtained as an insoluble solid due to strong π–π stacking. As a result, we directly applied column chromatography by using toluene/DCM/methanol (100:0:0 to 0:99:1) as eluent without concentrating the reaction mixture beforehand. After column chromatography, cyclophane **6** – resulting from a Cu^{I}-catalyzed click reaction[28] – was obtained in about 10% yield and characterized on the basis of ^{1}H NMR and high-resolution EI mass spectra.

Steady-state optical properties of **6** were investigated, which showed no solvent effects. The UV/Vis absorption spectrum of compound **6** in DCM was characterized by a very intense band centered at ca. 358 nm (ε = 42000 $\text{M}^{-1}\text{cm}^{-1}$) and 380 nm ($\varepsilon$ = 44000 $\text{M}^{-1}\text{cm}^{-1}$), which were assigned to the π→π* transition of the aromatic π-conjugated system in the molecule (Table 1, Figure 1a, black line). The addition of 15 equiv. of metal ions (Mg^{2+}, Hg^{2+}, Ba^{2+}, Zn^{2+}, Ca^{2+}, Co^{2+}, Cs^{+}, Fe^{3+}, K^{+}, Mn^{2+}, Na^{+}, Ni^{2+}, Cu^{2+}, Pb^{2+} as perchlorate salts) (2×10^{-2} M) in acetonitrile to 2 mL solutions of **6** (2×10^{-5} M) in DCM substantially altered the UV/Vis spectra for **6** (2×10^{-5} M, 2 mL). The presence of monovalent metal ions (Cs^{+}, K^{+}, Na^{+}) failed to influence the UV/Vis spectra of **6**. Alternatively, the UV/Vis spectra of **6** displayed 5–14 nm redshifts with bivalent and trivalent metal ions. The titration of **6** with various quantities of Mg^{2+}, Ba^{2+}, Hg^{2+}, Ca^{2+} and Zn^{2+} were performed (Supporting Information Figures S1–S4). A typical titration plot for Mg^{2+} is shown in Figure 1b. The absorption at 358 nm and 380 nm dramatically decreased with the gradual addition of Mg^{2+} to a solution of **6**, while a new set of bands centered at 368 (ε = 32000 $\text{M}^{-1}\text{cm}^{-1}$) and 388 nm ($\varepsilon$ = 33600 $\text{M}^{-1}\text{cm}^{-1}$) increased prominently with three isosbestic points at 363, 373 and 383 nm, which reached the maximum value at 7.5 equiv. of Mg^{2+}. The actual metal (M)/ligand (L) stoichiometry of binding for **6** and Mg^{2+} was found to be 1:2 (Supporting Information Figure S9). This was further supported by the IR results; IR absorbance of the carbonyl group in the macrocycle shifted from 1667 to 1663 cm^{-1} upon complexation with



Scheme 1. Synthesis scheme for the preparation of compound **6**. DMF = *N*,*N*-dimethylformamide; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.

Table 1. Photophysical properties and fluorescence lifetime data for the excimer band of **6** and **6** with Mg^{2+} (15 equiv.).

Entry	Sample	Absorption[a] λ_{max} [nm]	ε[a] [$\text{M}^{-1}\text{cm}^{-1}$]	Fluorescence[b] λ_{max} [nm]	Φ_{fl}[c]	Lifetimes τ_1 [ns]	τ_2 [ns]	χ^2
1	**6**	358, 380	44000	400	0.006	0.2	4.2	1.4
2	**6** and Mg^{2+}	368, 388	33600	480	0.009	14.9	4.2	1.1

[a] Measured in DCM solution (1.0×10^{-5} M). [b] Measured in DCM solution (1.0×10^{-5} M), upon excitation at the absorption maximum. [c] In DCM, *N*,*N*-bis(2-hydroperoxy-2-methoxyethyl)-1,4,5,8-naphthaldiimide (NP-III, Φ_{fl} = 0.01 in acetonitrile)[29] as the standard.

Mg^{2+} ion. Moreover, the ESI MS peak at *m*/*z* = 206.0 is consistent with a 1:2 ratio of the **6**/Mg^{2+} complex (Supporting Information). The optical properties of **6** and **6** with Mg^{2+} (15 equiv.) in DCM at room temperature are listed in Table 1.

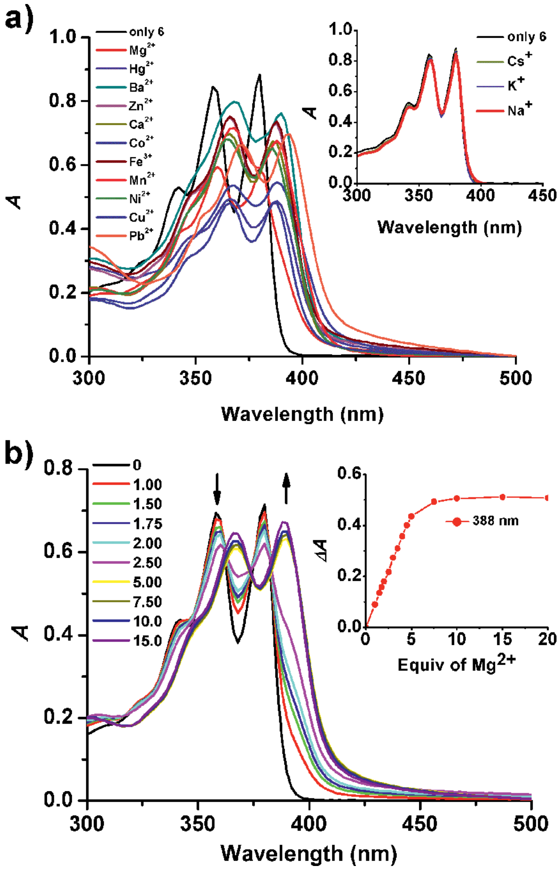


Figure 1. (a) UV/Vis absorption spectra of compound **6** (20 µM) upon addition of 15 equiv. of different metal ions (Mg2+, Hg^{2+}, Ba^{2+}, Zn^{2+}, Ca^{2+}, Co^{2+}, Cs^{+}, Fe^{3+}, K^{+}, Mn^{2+}, Na^{+}, Ni^{2+}, Cu^{2+}, Pb^{2+}) in a DCM/acetonitrile (1000:15, v/v) solution; (b) UV/Vis absorption titration spectra of compound **6** (20 µM) with Mg^{2+} (0, 1, 1.5, 1.75, 2, 2.5, 5, 7.5, 10, 15 equiv.) in a DCM/acetonitrile (1000:0–15, v/v) solution.

The fluorescence spectra of **6** in the presence of 15 equiv. of metal ions (Mg^{2+}, Hg^{2+}, Ba^{2+}, Zn^{2+}, Ca^{2+}, Co^{2+}, Cs^{+}, Fe^{3+}, K^{+}, Mn^{2+}, Na^{+}, Ni^{2+}, Cu^{2+}, Pb^{2+} as perchlorate salts) were recorded (Figure 2). The presence of Fe^{3+}, Co^{2+}, Ni^{2+} and Mn^{2+} enhanced the NDI emission at 400 nm, whereas Mg^{2+}, Ba^{2+}, Hg^{2+}, Ca^{2+}, Zn^{2+} and Pb^{2+} not only enhanced the emission at 400 nm but also led to a new excimer band at 480 nm. The other ions evaluated had little or no impact on the emission of **6**.

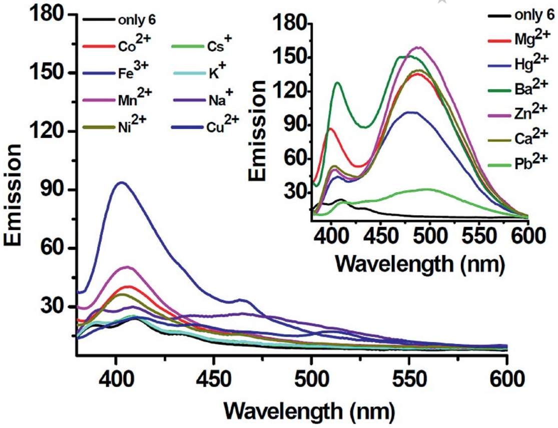


Figure 2. Fluorescence responses of compound **6** (20 µM) in the presence of 15 equiv. of various metal ions (Mg^{2+}, Hg^{2+}, Ba^{2+}, Zn^{2+}, Ca^{2+}, Pb^{2+}, Co^{2+}, Cs^{+}, Fe^{3+}, K^{+}, Mn^{2+}, Na^{+}, Ni^{2+}, Cu^{2+}) in a DCM/acetonitrile (1000:15, v/v) solution. Excitation wavelength was 360 nm with 5 nm slit widths.

A typical fluorescent titration experiment of **6** with Mg^{2+} is shown in Figure 3. After the addition of 1.5 equiv. of Mg^{2+}, a new emission at 480 nm appeared. In the presence of 10 equiv. of Mg^{2+}, the 480 nm emission band reached its maximum value. The time-resolved fluorescence spectra of **6** with (τ_1 = 14.9 ns, τ_2 = 4.2 ns) and without Mg^{2+} (τ_1 = 0.2 ns, τ_2 = 4.2 ns) were recorded in a DCM/acetonitrile (1000:15, v/v) solution at room temperature. The result indicated that the fluorescence lifetime ascribed to the dimer emission band (τ_1) was obviously elongated after the addition of Mg^{2+}. We also tested the fluorescence emission of **6** with various quantities of Ba^{2+}, Hg^{2+}, Ca^{2+} and Zn^{2+}, which showed similar results (Supporting Information, Figures S1–S8).

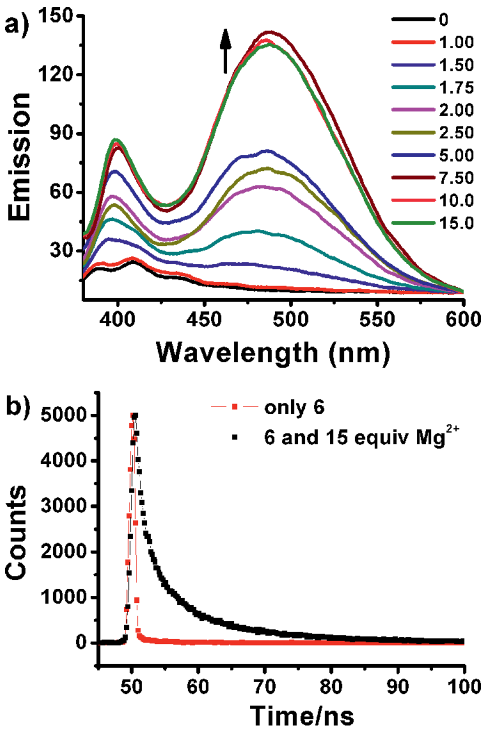


Figure 3. (a) Fluorescence titration spectra of compound **6** (20 µM) with Mg^{2+} (0, 1, 1.5, 1.75, 2, 2.5, 5, 7.5, 10, 15 equiv.) in a DCM/acetonitrile (1000:0–15, v/v) solution. λ_{ex} = 360 nm with 5 nm slit widths; (b) Time-resolved fluorescence spectra of **6** (2×10^{-5} M) in DCM with and without Mg^{2+} (15 equiv.) in a DCM/acetonitrile (1000:15, v/v) solution at room temp., λ_{ex} = 360 nm.

Time-dependent absorbance (λ_{max} = 388 nm) and fluorescence emission (λ_{max} = 480 nm) spectra of **6** and 15 equiv. of Mg^{2+} have been measured within 3 d, indicating the stability of the system (Supporting Information, Figures S10 and S11).

To gain more insight into the electron-transfer processes tuned by metal ions in this naphthalene-diimide cyclophane, DFT calculations of the molecular orbitals of **6** with and without metal ions were performed at the B3LYP/6-31G level by using the Gaussian 03 program.[30] The HOMO and LUMO orbitals from the calculation are depicted in Figure 4.

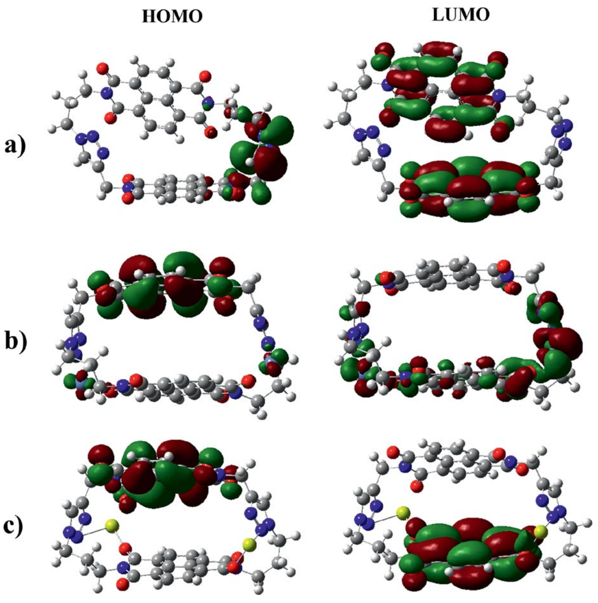


Figure 4. HOMO orbitals (left) and LUMO orbitals (right) of **6** (a), **6** after addition of Ni^{2+} (b) and **6** after addition of Mg^{2+} (c) obtained by using DFT calculations at the B3LYP/6-31G level.

For cyclophane **6** itself, the density in the HOMO is concentrated in the triazole moiety, while the density in the LUMO is mainly localized on the two NDI planes. It is expected that electron transfer from the triazole moieties to the NDI planes should lead to a weak emission of NDI (Figure 5, center). In the presence of Ni^{2+}, the largest coefficients in the HOMO are mainly localized on the NDI moiety, and the largest coefficients in the LUMO are mostly contributed by the two triazole units coordinated to Ni^{2+}. The results indicate that the electron-donating ability of the triazole units is weakened, which leads to a slight enhancement of the emission of the NDI moiety (Figure 5, left). However, for the complex of **6** with Mg^{2+}, the largest coefficients in the HOMO and the LUMO are both principally contributed by the NDI moiety, which supports the slight redshift of the UV/Vis absorptions in the ground state and the appearance of the dimer emission of NDI (Figure 5, right).

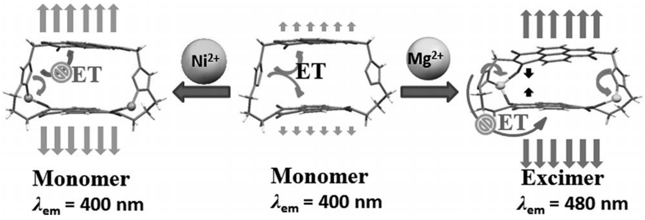


Figure 5. Schematic interpretation of the electron-transfer process tuned by metal ions.

Conclusions

We have synthesized a new NDI cyclophane and investigated the influence of metal ions on photoinduced electron transfer in this donor–bridge–acceptor system. This new scaffold enables: (i) the turning off of the photoinduced electron transfer from the triazole to the NDI moieties by divalent metal ions such as Mg^{2+}, Ba^{2+}, Hg^{2+}, Ca^{2+}, Zn^{2+} and Pb^{2+}, (ii) the turning on of the electron transfer between the NDI units at the same time, which leads to an enhanced dimer emission of the NDI. However, Fe^{3+}, Co^{2+}, Ni^{2+} and Mn^{2+} were found to only enhance the monomer emission of NDI. Such supramolecular systems are the basis for molecular electronic devices that can be potentially applied as optical switches, sensors and artificial photosynthetic systems.

Experimental Section

General Methods: ^1H and ^{13}C NMR spectra were obtained with a Bruker ARX400 spectrometer by using tetramethylsilane (TMS) as the internal standard, and chemical shifts (δ) are given in ppm relative to TMS. Matrix-assisted laser desorption/ionization reflectron time-of-flight (MALDI-TOF) mass spectrometry was performed with a Bruker Biflex III mass spectrometer. Elemental analyses were carried out with a Carlo Erba 1106 elemental analyzer. Melting points were obtained from TGA data recorded by using a DTG-60 SHIMADZU apparatus. Electronic absorption spectra were measured with a JASCO V-579 spectrophotometer. Fluorescence excitation and emission spectra were recorded by using a Hitachi F-4500 instrument. The fluorescence decay curves were determined by using an Edinburgh FLS-920 instrument with single-photon counting measurement. Accordingly, samples were irradiated with a Picoquant LDH-D-C-375 pulsed diode laser.

Materials: Synthesis of **6** employed chemicals and solvents that were reagent grade purchased from Aldrich, ACROS Chemical Co., and used without further purification. The silica gel (200–300 mesh) for column chromatography was purchased from JIYIDA Silica Gel Corp. in Qing Dao.

Spectroscopy Measurement: Solutions of compound **6** (2×10^{-5} M) were prepared with DCM (HPLC grade). The UV/Vis absorption spectra of compound **6** before and after addition of metal ions at room temp. in solution were measured; fluorescence emission spectra were measured with excitation at 360 nm. The fluorescence lifetimes of compound **6** before and after addition of 15 equiv. of Mg^{2+} were measured at room temp. in solution under deaerated conditions.

3-Azido-1-propylamine (2): To a stirred solution of **1** (5 g, 22.8 mmol) dissolved in water (16 mL) was added aqueous sodium azide (4.45 g, 68.5 mmol in 10 mL of water), and the mixture heated to 100 °C overnight. KOH pellets were added to bring the solution to basic pH, and the resulting solution was then extracted with diethyl ether (3 × 50 mL). The combined organic phases were dried with $MgSO_4$ and concentrated to give the desired amine **2** as a colourless volatile oil (2.05 g, 89.5% yield).[24]

***N,N′*-Bis(3-azidopropyl)-1,4,5,8-naphthalenetetracarboxdiimide (4):** Compound **3** (2.14 g, 8.0 mmol) and **2** (2.2 equiv.) were combined in DMF (40 mL). The mixture was stirred at 75 °C overnight. The resulting precipitate was filtered off, rinsed with acetone, and dried in a vacuum oven to give **4** as an analytically pure powder (2.8 g, 81.0% yield). M.p. 187–188 °C. IR (neat):$\tilde{\nu}_{max}$ = 2118 (N_3) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.78 (s, 4 H), 4.32 (t, J = 7.04 Hz, 4 H), 3.47 (t, J = 6.60 Hz, 4 H), 2.06 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.01, 131.31, 126.92, 126.73, 49.56, 38.67, 27.68 ppm. EI-MS: m/z = 404 [M – N_2]. $C_{20}H_{16}N_8O_4$ (432.40): calcd. C 55.55, H 3.73, N 25.91; found C 55.27, H 3.65, N 26.13.

***N,N′*-Bis(prop-2-ynyl)-1,4,5,8-naphthalenetetracarboxdiimide (5):** Compound **3** (4.02 g, 15 mmol) and 2-propyn-1-amine (2.2 equiv.) were combined in DMF (80 mL). The mixture was stirred at 65 °C overnight. The precipitate was filtered out, rinsed with acetone, and dried in a vacuum oven to give product **5** as an analytically pure powder (3.35 g, 65.0% yield).[26]

1,4,5,8-Naphthalenetetracarboxdiimide Derivative 6: To a stirred solution of copper(I) iodide (0.1 equiv.) and DBU (1.36 mL) dissolved in toluene (600 mL) under nitrogen was added dropwise a mixed solution of **4** (267 mg, 0.617 mmol) and **5** (211 mg, 0.617 mmol) in toluene, while the temperature was kept at 75 °C for 48 h. After another 3 d, TLC analysis showed that the reaction was complete. The white solid product **6** (47 mg, 10% yield) was obtained after direct column chromatography by using toluene/DCM/methanol (100:0:0 to 0:99:1) as eluent. M.p. > 300 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.85 (s, 4 H), 7.84 (s, 2 H), 7.71 (s, 4 H), 5.55 (s, 4 H), 4.48 (t, J = 4.00 Hz, 4 H), 3.99 (t, J = 6.48 Hz, 4 H), 2.36 (m, 4 H) ppm. HRMS (EI): calcd. for $C_{40}H_{26}N_{10}O_8$ 774.1935; found 774.1945. ^{13}C NMR spectra of **6** were not well resolved due to poor solubility.

Supporting Information (see footnote on the first page of this article): Characterization data for all key intermediates and the final product, UV/Vis spectra and fluorescence spectra of compound **6** with metal ions, ^1H and ^{13}C NMR spectra for key intermediates, ^1H NMR and HR-EI mass spectra of **6**.

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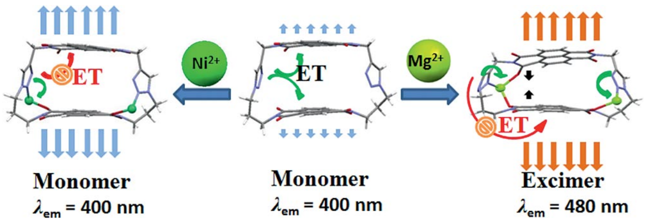
Cyclophane-Modulated Electron Transfer



A new naphthalene-diimide cyclophane was synthesized, and the tuning of photoinduced electronic transfer in this cyclophane by metal ions was investigated. Monomer or dimer emission of naphthalenetetracarboxdiimide (NDI) was observed in the presence of different divalent metal ions.

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Synthesis of a Naphthalene-diimide Cyclophane for Tuning Supramolecular Interactions by Metal Ions

Keywords: Click reaction / Triazole / Naphthalene diimide / Cyclophanes / Fluorescence / Electron transfer