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# A Boat-Shaped Tetracationic Macrocycle with a Semiconducting Organic Framework

Minh T. Nguyen, Matthew D. Krzyaniak, Magdalena Owczarek, Daniel P. Ferris, Michael R. Wasielewski, and J. Fraser Stoddart\*

Abstract: We report the synthesis of a tetracationic macrocycle which contains two N,N'-bis(methylene)naphthalenediimide units inserted in between the pyridinium rings of the bipyridinium units in cyclobis(paraquat-p-phenylene) (CBPQT<sup>4+</sup> or "blue box") and describe the investigation of its potential use in materials for organic electronics. The incorporation of the two naphthalenediimide (NDI) units into the constitution of  $CBPQT^{4+}$ , not only changes the supramolecular properties of the tetracation in the solid state, but also has a profound influence on the electrochemical and electronic behavior of the resulting tetracationic macrocycle. In particular, the solid-state (super)structure, investigated by single-crystal X-ray diffraction, reveals the formation of a three-dimensional (3D) supramolecular framework with ca. 2.8 nm diameter onedimensional (1D) hexagonal channels. Electrochemical studies on solid-state thin films of the macrocycle show that they exhibit semiconducting properties with a redox-conductivity of up to  $7.6 \times 10^{-4}$  Sm<sup>-1</sup>. Moreover, EPR and ENDOR spectroscopies show that charge is equally shared between the NDIs within the one-electron reduced state of the NDI-based macrocycle on the time scale of these techniques.

**O**rganic polycationic cyclophanes, especially those capable of hosting electron-rich guests by dint of donor-acceptor interactions, have been employed<sup>[1]</sup> widely over the past few decades in a number of different contexts. The scientific community find these cyclophanes attractive, not only because of the role they play as electron-deficient receptors in molecular recognition processes,<sup>[2]</sup> but also on account of their usefulness as building blocks for the construction of more complex systems, i.e., mechanically interlocked molecules (MIMs) such as catenanes,<sup>[3]</sup> rotaxanes,<sup>[4]</sup> and catenanerotaxane-containing supramolecular architectures.<sup>[5]</sup> or Among these organic polycationic cyclophanes, pyridiniumand imidazolium-based systems are the two most commonly studied classes. The former compounds have been explored widely for applications in molecular recognition<sup>[6]</sup> and molecular machines, including switches,<sup>[7]</sup> attenuators,<sup>[8]</sup> and memory devices.<sup>[9]</sup> The later compounds-imidazoliumbased cyclophanes, recently reported by Sessler and coworkers<sup>[1b]</sup> as "Texas-sized or burnt orange molecular boxes" (Figure 1)—have also been investigated in the context of anion recognition<sup>[10]</sup> and as supramolecular organic frameworks.<sup>[11]</sup>



Figure 1. Structural formulas of CBPQT<sup>4+</sup> or "blue box", the Texassized or "burnt orange box", and  $NDITM^{4+}$  reported in this study.

Despite their long history in supramolecular chemistry, organic polycationic macrocycles have not been investigated extensively as materials with potential use in organic electronics, such as organic field-effect transistors (OFETs) and/ or photovoltaics. One of the obstacles, for cationic cyclophanes in general, is the Coulombic repulsion between the positively charged units in these macrocycles. The intrinsic repulsion prevents intermolecular stacking and results in materials devoid of the facile conductivity characteristics of organic semiconductors.<sup>[12]</sup>

Recent studies in our laboratory have revealed,<sup>[13]</sup> however, that the reduction of a pyridinium-based tetracationic cyclophane—cyclo-bis(paraquat-p-phenylene)<sup>[14]</sup> (CBPQT<sup>4+</sup> "blue box")-to its bis-radical dicationic state or  $[CBPQT^{2(+)}]$  facilitates the formation of an inclusion complex with the methyl viologen (MV<sup>++</sup>) radical cation. This complex, which exhibits intermolecular stacking in the solid state through radical-radical interactions,<sup>[13]</sup> has been considered as a candidate for use in OFETs.<sup>[15]</sup> Although the reduced solidstate superstructure is stable under ambient conditions for weeks, oxidation back to the tetracationic state would, however, induce molecular repulsion and device degradation, limiting its long-term operation in air under ambient conditions. We anticipated that incorporating air-stable building blocks, which exhibit intermolecular  $\pi$ -stacking, into tetracationic cyclophanes could increase the viability of these systems as long-lasting molecules for electronic devices. In addition, the electron-deficient characteristics associated with tetracationic cyclophanes might also be beneficial when

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<sup>[\*]</sup> Dr. M. T. Nguyen, Dr. M. D. Krzyaniak, Dr. M. Owczarek, Dr. D. P. Ferris, Prof. M. R. Wasielewski, Prof. J. F. Stoddart Department of Chemistry, Northwestern University 2145 Sheridan Road, Evanston, IL 60208 (USA) E-mail: Stoddart@northwestern.edu

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the author(s) of this article can be found under: https://doi.org/10.1002/anie.201702019.

intergrated into organic semiconductors since they would result in a material with high electron affinity, thereby increasing the air-stability of the materials during cycling operations.<sup>[16]</sup>

Herein, we report the design, synthesis, and characterization of a novel organic tetracationic macrocycle (**NDITM**<sup>4+</sup>) that has naphthalenediimide units (**NDIs**) components used in the preparation of many organic semiconductors<sup>[17]</sup>—incorporated into the constitution of CBPQT<sup>4+</sup>. The macrocycle was designed so that both the organic-electronic properties inherent in the NDI units and the electron-deficient nature of a tetracationic cyclophane could be utilized simultaneously to produce an air-stable system for potential use as an organic semiconductor. The incorporation of two NDIs into the "blue box" archetype has resulted in a novel tetracationic macrocycle **NDITM**<sup>4+</sup> which exhibits a unique kind of self-assembly to afford a supramolecular organic framework that displays semiconducting properties with high electron affinity in the solid state.

The synthesis of **NDITM**<sup>4+</sup> was carried out using a wellestablished synthetic approach (Scheme 1) for the preparation of cationic macrocycles. The starting material in the synthesis—bis(4-pyridylmethyl)naphthalenediimide

(PMNDI)-was prepared from an imide condensation between naphthalene-1,4:5,8-tetracarboxy dianhydride and 4-(aminomethyl)pyridine in DMF at 130°C overnight. Reaction of PMNDI with 1,4-bis(bromomethyl)benzene, followed by anion exchange from bromide to hexafluorophosphate ions in aqueous MeOH, yielded the dibromide  $DB \cdot 2PF_6$ . The final cyclization to produce NDITM<sup>4+</sup> involves the reaction of DB·2PF<sub>6</sub> with 1 equiv of PMNDI in the presence of tetrabutylammonium iodide (TBAI) as a catalyst. The tetracationic macrocycle was precipitated from an aqueous solution of NH<sub>4</sub>PF<sub>6</sub>, collected, and purified by column chromatography (SiO<sub>2</sub>: 0.5 % NH<sub>4</sub>PF<sub>6</sub> in Me<sub>2</sub>CO) to yield NDITM 4PF<sub>6</sub>. Reverse-phase analytical HPLC of this compound using a H<sub>2</sub>O/MeCN (0.1 % TFA) gradient elution revealed a presence of pure **NDITM**<sup>4+</sup> eluting with a 32 min retention time (Figure S1, Supporting Information). High resolution electrospray ionization-mass spectrometric (ESI-MS) analysis indicated the existence of the NDITM 4PF<sub>6</sub> with the loss of 2-4  $PF_6^-$  counterions, i.e.,  $[M-2PF_6]^{2+}$  and  $[M-3PF_6]^{3+}$  were



**Scheme 1.** Synthesis of **NDITM**<sup>4+</sup>. Reagent and conditions: (i) 1) 1,4-Bis (bromomethyl)benzene/DMF/110 °C/5 h, followed by 2) NH<sub>4</sub>PF<sub>6</sub>/H<sub>2</sub>O. (ii) 1) PMNDI/TBAI/DMF/120 °C/24 h, followed by 2) NH<sub>4</sub>PF<sub>6</sub>/H<sub>2</sub>O.

detected (Figure S2) in the gas phase at m/z = 697.113 and 416.442, respectively. Both the <sup>1</sup>H and <sup>13</sup>C NMR spectra of **NDITM**·4PF<sub>6</sub> support the existence of a single and highly symmetrical compound in which the assignments of all the resonances were confirmed (Figure S3 to S7) by two-dimensional <sup>1</sup>H-<sup>1</sup>H and <sup>1</sup>H-<sup>13</sup>C correlation spectroscopy experiments.

The solid-state (super)structure (Figure 2a and S8) of **NDITM**<sup>4+</sup>, which was determined unambiguously by X-ray diffraction analysis of a single crystal obtained by the slow evaporation of NDITM 4PF<sub>6</sub> solution in MeCN during 3 days, reveals a tetracation with a boat-like conformation. Two crystallographically equivalent NDI units are positioned in the hull of the boat conformation, separated by 4.6 Å (defined by the distance between the two closest hydrogen atoms), and have a dihedral angle of 135° relative to each other (Figure S11). Unlike the solid-state structure (Figure S13) of the precursor **DB**<sup>2+</sup> and other **PMNDI**-containing molecules,<sup>[18]</sup> all pyridinium units in NDITM<sup>4+</sup> are oriented (Figure S12) toward the same side relative to the NDI unit to which they are connected, supporting a dihedral angle of 68°. This conformation is not only commensurate with the formation of the macrocycle, but it also facilitates the face-to-face intermolecular  $\pi$ - $\pi$  stacking for NDI units (see below). The solidstate superstructure of NDITM<sup>4+</sup> reveals that it crystallizes in the hexagonal space group  $P6_3/m$  and forms (Figure 2a) a porous network with one-dimensional (1D) channels of ca. 28 Å in diameter. Since solvent molecules and some of the PF6- counterions are disordered and exhibit partial occupancy in these relatively large pores, they have been eliminated during the refinement using an implemented program in the crystallographic software.<sup>[19]</sup> Each hexagonal channel is comprised of two alternating layers each containing three NDITM<sup>4+</sup> macrocycles that are positioned such that every macrocycle establishes eight sets of short contacts with four of its neighbors through [N<sup>+</sup>...O=C] (mean  $d_{N...O}$ = 3.14 Å) and [C–H···O] (mean  $d_{C··O} = 3.14$  Å) interactions (Figure S12). Using these weak interactions, two repeated sets of three NDITM<sup>4+</sup> macrocycles are stacked in a coaxial manner with a perpendicular rotation angle of 60° forming an infinite hexagonal channel (Figure 2b). These 1D channels are held together by  $\pi$ - $\pi$  interactions ( $d_{\text{NDI-NDI plane-plane}} =$ 3.35 Å, Figure 2c) between the NDI units. Consequently, a three-dimensional (3D) superstructural framework with infinite 1D channels (pore diameter ca. 20 Å) along the *c*-axis is formed. The incorporation of NDI units plays a critical role in the formation of this supramolecular organic framework. These units are involved, not only in intermolecular  $\pi$ - $\pi$ stacking, but also in short contacts between the carbonyl groups and the bis(pyridinium)phenylene fragments.

The intermolecular  $\pi$ - $\pi$  interactions of NDI units along the *c*-axis in the solid-state superstructure of **NDITM**<sup>4+</sup>, combined with charge hopping between the two NDI units within the same **NDITM**<sup>4+</sup> macrocycle (see below), implies that electron transport could be occurring along this 1D direction as NDI  $\pi$ - $\pi$  stacking and charge hopping are known<sup>[17]</sup> to cause increased charge mobility in n-type organic semiconductors. In order to investigate the electronic properties induced by the NDI units, we have examined the

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**Figure 2.** a) Graphical representations of the single-crystal X-ray (super)structure of **NDITM**<sup>4+</sup> showing the assembly into a 3D framework with relatively large 1D channels. The SEM insert shows the extended hexagonal shape of one microscopic crystal. b) Plan and side-on views of a representative 1D channel that has two consecutive layers (blue alternating with yellow and back) containing three **NDITM**<sup>4+</sup> macrocyles as a cyclic array in each layer. c) Side-on (left) and plan (right) views of the NDI stacks which propagate the extension of the 1D hexagonal channels to afford a 3D framework. Counterions and hydrogen atoms have been omitted for the sake of clarity.

electrochemical properties of NDITM<sup>4+</sup> at the molecular level by carrying out cyclic voltammetry (CV) on this tetracationic macrocycle. Two NDI reference compounds (Figure 3)—one neutral (NRef) and the other dicationic  $(\mathbf{CRef}^{2+})$ —were also investigated in order to explore the effects of both cyclization and the presence of the positive charges on the redox properties of NDI units (see the SI). The CV of NRef displays two reversible redox waves for NDI at -593 and -1050 mV vs. Ag/AgCl, corresponding to the formation of NDI- radical anions and NDI2- dianions, respectively. On account of the effect of the positive charges on the pyridinium units, the first reduction peak of  $\mathbf{CRef}^{2+}$  is shifted ca. 158 mV to a more positive potential (-435 mV), while the second reduction (-830 mV) is quasi-reversible and can be assigned to the reduction of the pyridinium units. See the SI for the details of the assignments. On the other hand, the CV of NDITM<sup>4+</sup> exhibits three reversible reduction peaks at -350, -820, and -1056 mV which can be assigned, respectively, to 1) the formation of NDI radical anions, 2) the reduction of the pyridinium rings, and 3) the reduction of the NDI radical anions to dianions. The significant anodic shift of the first reduction peak in the CV of NDITM<sup>4+</sup>, compared to that of either NRef ( $\Delta E = 240 \text{ mV}$ ) or CRef<sup>2+</sup>  $(\Delta E = 85 \text{ mV})$ , reveals the influence of both the positive charge and the macrocyclic ring formation on the electron affinity of the system. The lowest unoccupied molecular



*Figure 3.* Cyclic voltammograms of **NRef** (a), **CRef**<sup>2+</sup> (b), and **NDITM**<sup>4+</sup> (c) recorded at a 100 mVs<sup>-1</sup> scan rate using a Pt working electrode in 0.1  $\mu$  TBAPF<sub>6</sub>/MeCN electrolyte.

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orbital (LUMO) energy of **NDITM**<sup>4+</sup> was estimated to be -4.20 eV using the equation<sup>[20]</sup>  $E_{\text{LUMO}} = -4.8 - (E_{\text{red, onset}} - E_{\text{ferrocene}}) \text{ eV}$ . This low-lying LUMO level indicates that **NDITM**<sup>4+</sup> is a strong electron-accepting macrocycle and promising for use as an n-type organic semiconductor.

In order to probe the extent of possible electron hopping within **NDITM<sup>4+</sup>** as arising from it being a macrocycle, electron paramagnetic resonance (EPR) spectroscopy was performed on the NDITM<sup>(3+)</sup> and CRef<sup>(+)</sup> reduced states which are generated (Figure S15) by reacting the cationic compounds with Zn dust in MeCN. The CW-EPR spectrum (Figure 4a) of **CRef**<sup>(+)</sup> and corresponding simulation agree well with previously reported<sup>[21]</sup> EPR spectrum and hyperfine coupling values for a NDI radical anion, where the unpaired electron spin density is localized to a single NDI unit. The EPR spectrum (Figure 4b) of the  $NDITM^{(3+)}$  radicals and simulation, on the other hand, show a broadening and loss of hyperfine features, a change consistent with the unpaired spin density shared across two NDI units. An electron-nuclear double resonance (ENDOR) experiment was performed in order to confirm the proton hyperfine coupling values used in the simulation of the CW-EPR spectrum of **NDITM**<sup>(3+)</sup>. The <sup>1</sup>H CW-ENDOR spectrum (Figure 4c) of **NDITM**<sup>(3+)</sup> and simulation reveal an electron-to-proton hyperfine coupling constant of 2.65 MHz. This value is about one half of the hyperfine coupling constant found<sup>[22]</sup> for radicals localized on a single NDI unit, indicating that the unpaired electron hops between the two NDI units at a rate exceeding the ENDOR experiment timescale<sup>[22]</sup> (ca.  $10^7 \text{ s}^{-1}$ ).



**Figure 4.** CW-EPR Spectra of the **CRef**<sup>(+)</sup> (a) and **NDITM**<sup>(3+)</sup> (b) radicals, generated by reducing the cationic compounds with Zn dust in MeCN, recorded at 298 K. The corresponding simulations are overlaid in black. The hyperfine coupling constants (in MHz) used for the simulations are provided. c) <sup>1</sup>H CW-ENDOR spectrum of **NDITM**<sup>(3+)</sup> radicals at 246 K.

In order to glean information regarding charge hopping and molecular interactions of **NDITM**<sup>4+</sup> under conditions that are more relevant to organic electronics/devices, the electrochemical and electronic properties of the macrocycle were investigated as solid thin films. Thanks to the exclusive solubility of **NDITM**·4PF<sub>6</sub> in MeCN, thin films prepared by solution processing from a MeCN solution can be characterized electrochemically in CH<sub>2</sub>Cl<sub>2</sub>—a very poor solvent for **NDITM**·4PF<sub>6</sub>—without dissolvation from the surface. A scanrate dependence study of a **NDITM**·4PF<sub>6</sub> thin film, drop-cast from a MeCN solution onto a Pt electrode, was recorded (Figure S16) in a  $CH_2Cl_2$  electrolyte at scan rates in the 25–400 mV s<sup>-1</sup> range. The linear relationship between the peak current of the oxidation/reduction and the scan rates reveals that the solid-state thin films of **NDITM**·4PF<sub>6</sub> are highly electroactive and porous to the charge-compensating ions under these conditions,<sup>[23]</sup> a feature which is commonly observed in organic semiconductive thin films. This observed electroactive characteristic led us to investigate the electronic properties by determining the electrical conductivity of the **NDITM**·4PF<sub>6</sub> thin film using a Pt interdigitated electrode array (IDA, Figure 5 a and b). Films of varying thickness were



**Figure 5.** a) Photographs of a Pt-interdigitated electrode array (IDA) used in the in situ conductivity measurements. b) Schematic illustration of the conductivity measurement setup using a 10  $\mu$ m Pt IDA. c) Solid-state CV and in situ conductivity of **NDITM**-4PF<sub>6</sub> thin film.

prepared by spin coating NDITM 4PF<sub>6</sub> from a MeCN solution. The conductivity of the film was calculated using a wellestablished relationship between the observed drain current and the bulk material conductivity.<sup>[24]</sup> See Equation (1) in the SI. The solid-state CV and the potential-dependent conductivity profile of a 500 nm thick  $NDITM \cdot 4PF_6$  film were recorded (Figure 5c) in CH<sub>2</sub>Cl<sub>2</sub>. The first conductivity peak appears at -426 mV vs. Ag/AgCl which is approximately the same potential as the first reduction peak observed in the solid-state CV. The significant increase in conductivity can be attributed to the generation of mobile radicals on the NDI units upon reduction. The second, more negative and larger magnitude, peak in the conductivity profile appears at ca. -1121 mV and has a global maximum conductivity of  $7.6 \times$  $10^{-4} \,\mathrm{Sm^{-1}}$ . This maximum conductivity was observed for **NDITM**·4PF<sub>6</sub> in a reduced state in which the macrocycle has the highest possible number of radicals per macrocycle (Figure S18), consistent with an increase in the conductivity of an organic semiconductor upon chemical doping<sup>[25]</sup> to generate free charge carriers. Although these measurements show conductivity values of one-to-three order(s) of magnitude lower than those for conducting polymers and/or some NDI-based materials,<sup>[24g,26]</sup> the fact that the solid-state superstructure is composed of a large-pore framework, while the

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conductivity values are still comparable to materials used in many organic electrodes,<sup>[27]</sup> suggests a potential use for this tetracationic macrocycle as an organic semiconductor.

In summary, we have prepared a novel naphthalenediimide-based tetracationic macrocycle, which not only adopts a unique (super)structure, but also displays semiconductive properties with high electron affinity (4.2 eV) in the solid state. The self-assembly, driven by  $[N^+...O=C]/$ [C-H...O] and  $\pi$ - $\pi$  stacking interactions of naphthalenediimide units, facilitates the formation of a 3D organic framework with 1D hexagonal channels having diameters of ca. 2.8 nm. A maximum redox-conductivity of  $7.6 \times 10^{-4}$  Sm<sup>-1</sup> was observed for a thin film of this tetracationic macrocycle, implying that it could find potential applications when incorporated into organic electronics.

#### **Experimental Section**

NDITM-4PF<sub>6</sub>. N,N-Bis(4-pyridylmethyl)naphthalenediimide (PMNDI, 224 mg, 0.5 mmol) was stirred in dry DMF at 120°C under a N2 atmosphere until all solid had completely dissolved. A solution of **DB**·2PF<sub>6</sub> (553 mg, 0.5 mmol) and TBAI (37 mg, 20 % mol) in dry DMF (20 mL) was added quickly to the above solution. The reaction mixture was heated under N2 at 120 °C for 1 day and cooled to room temperature. The yellow precipitate was collected by vacuum filtration and dissolved in a 1:1 mixture of H<sub>2</sub>O/MeOH (300 mL). An excess of  $NH_4PF_6$  was added to the solution, resulting in the formation of a white solid which was collected by centrifugation, washed with  $H_2O$  (3 × 20 mL), MeOH (1 × 20 mL) and dried in vacuo. The crude product was purified using column chromatography (SiO<sub>2</sub>: 0.5% NH<sub>4</sub>PF<sub>6</sub> in Me<sub>2</sub>CO) and the organic solvents were removed by rotary evaporation. The product was washed with H<sub>2</sub>O to remove NH<sub>4</sub>PF<sub>6</sub> and dried in vacuo to yield a white, crystalline solid NDITM-4PF<sub>6</sub> (290 mg) in 35% yield. <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>CN, 298 K):  $\delta = 8.75$  (s, 8H), 8.64 (d, J = 6.9 Hz, 8H), 8.00 (d, J = 6.9 Hz, 8H), 7.45 (s, 8H), 5.67 (s, 8H), 5.54 ppm (s, 8H). <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>CN, 298 K):  $\delta = 164.0$ , 159.0, 145.2, 135.8, 132.0, 130.8, 127.93, 127.8, 127.8, 64.4, 44.2 ppm. ESI-HRMS calcd for  $[M-2PF_6]^{2+} m/z =$ 697.143 and  $[M-3PF_6]^{3+}$  m/z = 416.442, found 697.143 and 416.442, respectively.

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#### **Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** electron transport · macrocycles · molecular electronics · organic frameworks · organic semiconductors

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## **Communications**

**Organic Semiconductors** 

M. T. Nguyen, M. D. Krzyaniak, M. Owczarek, D. P. Ferris, M. R. Wasielewski, J. F. Stoddart\* \_\_\_\_\_

A Boat-Shaped Tetracationic Macrocycle with a Semiconducting Organic Framework



**Organic electronics**: A tetracationic macrocyle containing two naphthalenediimide (NDI) units and four pyridinium rings was synthesized and investigated for its potential use as an organic semiconductor. The incorporation of the NDI units into the constitution of cyclobis-(paraquat-*p*-phenylene) has resulted in a macrocyle that exhibits a boat-shape conformation and assembles into an ultralarge-pore supramolecular framework with semiconducting properties.