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X-Shaped Oligomeric Pyromellitimide Polyradicals

Yilei Wu,^{1,2†} Ji-Min Han,^{1†} Michael Hong,^{1†} Matthew D. Krzyaniak,^{1,2,3} Anthea K. Blackburn,¹

Isurika R. Fernando,¹ Dennis D. Cao,¹* Michael R. Wasielewski,^{1,2,3}* J. Fraser Stoddart¹*

¹Department of Chemistry, ²Argonne-Northwestern Solar Energy Research (ANSER) Center, and ³Institute for Sustainability and Energy at Northwestern, Northwestern University, Evanston IL 60208-3113

ABSTRACT: The synthesis of stable organic polyradicals is important for the development of magnetic materials. Herein, we report the synthesis, isolation, and characterization of a series of X-shaped pyromellitimide (PI) oligomers (X_n -R, n = 2-4, R = Hex or Ph) linked together by single C-C bonds between their benzenoid cores. We hypothesize that these oligomers might form high-spin states in their reduced forms because of the nearly orthogonal conformations adopted by their PI units. ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopies confirmed the isolation of the dimeric, trimeric, and tetrameric homologues. X-Ray crystallography shows that X_2 -Ph crystallizes into a densely packed superstructure, despite the criss-crossed conformations adopted by the molecules. Electrochemical experiments, carried out on the oligomers X_n -Hex, reveal that the reductions of the PI units occur at multiple distinct potentials, highlighting the weak electronic coupling between the adjacent redox centers. Finally, the chemically generated radical anion and polyanion states, X_n -Hex⁻ and X_n -Hexⁿ⁽⁻⁾</sup>, respectively, were probed extensively by UV-Vis-NIR absorption, EPR and electron nuclear double resonance (ENDOR) spectroscopies. The ENDOR spectra of the radical monoanions X_n -**Hex**⁻ reveal that the unpaired electron is largely localized on a single PI unit. Further reductions of X_n -Hex⁻ yield EPR signals (in frozen solutions) that can be assigned to spin-spin interactions in X_2 -Hex²⁽⁻⁾, X_3 -Hex³⁽⁻⁾, and X_4 -Hex⁴⁽⁻⁾. Taken together, these findings demonstrate that directly linking the benzene rings of PIs with a single C-C bond is a viable method for generating stabilized high-spin organic anionic polyradicals.

The search for organic molecules having large numbers of magnetically ordered unpaired spins leading to molecular magnets has a long history focused on polyradicals, polycarbenes, and organometallic complexes.¹⁻²¹ Polyradicals of aromatic diimides represent a class of molecules that has received much less attention²²⁻²⁶ despite having been utilized to create thermally and chemically stable materials for applications, ranging from car paints to high-temperature adhesives and insulators,²⁷ organic-electrode batteries,²⁸⁻³² ion-transport channels, ³³⁻³⁴ organic photovoltaics,³⁵⁻³⁶ and other organic electronics.^{35,37} These applications are enabled by the two reversible one-electron reduction processes that aromatic diimides typically undergo to form, first of all, a radical anion and then subsequently a spin-paired dianion.²⁷ Each of these redox states has a characteristic optical signature along with unique electrochemical and photophysical properties that can be leveraged in applications.³⁸⁻⁴⁰ Investigations into this class of compounds have been bolstered by the fact that a myriad of N-functionalized aromatic imide derivatives can be produced²⁷ by reacting the corresponding anhydrides or carboxylic acids with almost any primary amine. In the larger aromatic diimides, core functionalization has proven to be a viable strategy for controlling molecular packing, introducing solubilizing groups, and tuning orbital energy levels.^{37,41-45} Directly coupled naphthalene diimide oligomers have been shown by Polander et al.⁴⁶ to be amenable to incorporation into organic field-effect transistors. These corefunctionalization strategies have not been applied widely to the smallest of the diimides, namely pyromellitimide (PI), despite the low molecular weights of PIs, which are attractive in organic electronics applications where efficient charge-to-mass ratios are crucial for device utility.^{29,35} Recently, we reported the synthesis of the parent 3,6-dihalo-PIs,⁴⁷ which exhibit significant twopoint halogen bonding interactions in the solid state.⁴⁸⁻⁴⁹ We envisioned that these 3,6-dihalo-PIs

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could be readily transformed into core-functionalized PI compounds. Indeed, 3,6-dibromo-PI derivatives were utilized by Guo *et al.*⁵⁰ as the starting point for the synthesis of a series of donor-acceptor poly(phenyleneethynylene)s. In these mixtures, which showed broad absorption profiles, the PI units were spaced apart by bisethynylaryl donors to create a phenylethynylene backbone. Independently, Rhee *et al.*⁵¹ have reported that dehalogenative coupling of 3,6-dibromo-PIs produces a solution-processible polydisperse mixture that could be cast into thin films.

We hypothesized that directly core-coupled oligo-PI compounds would display attractive selfassembly, electrochemical, photophysical and magnetic properties. Therefore, we have sought to obtain and evaluate these PI oligomers. Herein, we describe the synthesis and isolation of a series of torsionally frustrated PI oligomers X_n -R—where *n* is the number of PI units (n = 2-4) and **R** is the functional group attached to the nitrogen atoms—in which the PI units are coupled directly together by C–C bonds between their benzenoid rings. Additionally, we report (i) the Xray crystal structure of X_2 -Ph, (ii) the electrochemical behavior of the oligomers X_n -Hex, (iii) the UV-Vis-NIR absorption, EPR and electron nuclear double resonance (ENDOR) spectra of the chemically generated radical monoanionic and dianionic states of X_2 -Hex, and (iv) present evidence for the formation of spin multiplets ($S > \frac{1}{2}$) upon multiply reducing X_n -Hex.

RESULTS AND DISCUSSION

Synthesis. 3-Bromo-PIs **1-R** were synthesized following a similar protocol to the one that was used to produce the dihalo-3,6-PIs in our previous report.⁴⁷ Briefly, commercially available 3-bromo-1,2,4,5-tetramethylbenzene was oxidized with KMnO₄ to yield the tetracarboxylic acid, which was dehydrated by Ac_2O and reacted with hexylamine or aniline to yield **1-Hex** and **1-Ph**,

respectively (Scheme S1). We hypothesized that by subjecting 1 to a homocoupling reaction (Scheme 1), we could produce torsionally frustrated compounds (X_n-R) that could potentially



Scheme 1. Synthesis of X_n -R compounds. (a) Ullman coupling of the monobromide 1-R alone yields X_2 -R whereas (b) exposing a mixture of mono- and dibromides 1-R and 2-R to the same conditions yields oligomers X_n -R (n = 2-4). R = C₆H₁₃ or Ph. Reaction conditions: (i) Activated Cu Bronze, NMP, 150 °C for 3.5 h.

exhibit weak to moderate electronic coupling and stabilization over multiple imide sites. Inspection of molecular models of X_2 -Hex revealed that it is impossible for the aryl–aryl bond to experience free rotation as a consequence of significant steric and electronic repulsions between the imide carbonyl oxygen atoms. Initial attempts to conduct the Ullman coupling of 1-Hex utilizing anhydrous DMF as solvent produced in 81% yield a bright orange side-product, which was identified to be an undesired dimethylamination byproduct. No oligomeric pyromellitimides were isolated. Through the course of reaction optimization, it was found that NMP was a suitable replacement solvent for DMF. MALDI mass spectrometry of the crude reaction mixture after Ullman homocoupling of 1-Hex in NMP did not display any bromine isotope patterns,

suggesting completion of the reaction and consumption of the starting material. Purification by preparative TLC yielded X_2 -Hex, in addition to the reduction byproduct *N*,*N*'dihexylpyromellitimide (PI-Hex), in 30 and 37% yields, respectively. Subsequently, we sought to synthesize the higher order oligomers X_n -R. We envisioned that by conducting the Ullman coupling on a mixture of mono- and dibromo-PIs, the distribution of products could be controlled statistically. MALDI mass spectrometry performed (Figure S1) on the crude mixture, obtained after reacting 1-Hex with 2-Hex in a 2:1 ratio under Ullman coupling conditions, revealed the presence of oligomers up to nine PI units in length. After purification by either preparative GPC or TLC, we were able to isolate the monomeric, dimeric, trimeric, and tetrameric products, which we designate as having the constitutions PI-Hex, X_2 -Hex, X_3 -Hex, and X_4 -Hex, respectively.

NMR Spectroscopy. These constitutional designations were confirmed by NMR spectroscopy. In the ¹H NMR spectra (Figure 1a) of these compounds, the ratio of the integrals of the terminal PI core proton resonances to those of the NCH protons alpha to the imide nitrogen atoms correspond to the assigned number of PI units. In X_3 -Hex and X_4 -Hex, two different triplet resonances are observed around 3.5 ppm in the spectrum on account of the differences in chemical environments between the "outer" and "inner" PI units leading to constitutional heterotopicity between the *N*-methylene protons. A downfield shift of the terminal PI core proton resonances is observed with increasing oligomer lengths. This observation can be rationalized by the inductive electron-withdrawing effects of the imide groups on the additional linked PI units, thus further confirming the direct coupling of these units. Unsurprisingly, the magnitude of this signal shift is found to be much smaller between X_3 -Hex and X_4 -Hex, than it is between PI-Hex

and X_2 -Hex, because the additional PI units in the larger oligomers are further away from the terminal aromatic protons. The carbonyl region of the ¹³C NMR spectra (Figure 1b) clearly reveals the increasing number of heterotopic imide carbon atoms with increasing oligomer lengths.

Figure 1. Selected portions of the ¹H and ¹³C NMR spectra of **X**₄-**Hex**, **X**₃-**Hex**, **X**₂-**Hex**, and **PI-Hex**, from top to bottom. The top half of the structural formulas, which are related by rotation about a C_2 axis (gray dashed line), are not depicted for the sake of clarity. (a) The ratio of integrations of the core (blue) and alpha-carbon (green and red) proton resonances in the ¹H NMR spectra correspond to constitutionally heterotopic "inner" and "outer" PI units. (b) The expected number of resonances are also observed for the carbonyl carbon atoms in the ¹³C NMR spectra.

X-Ray Crystallography. In order to gain further insight into the conformations adopted by these oligomeric pyromellitimides, we turned our attention to obtaining solid-state structures. Initial attempts to crystallize X_n -Hex were unsuccessful, no doubt as a consequence of the relatively

flexible alkyl chains. Hence, we synthesized X_2 -Ph starting from 1-Ph, following the same protocols (Scheme 1a) as described for X_2 -Hex. Purification of the longer *N*-phenylated derivatives X_n -Ph, obtained following the protocol outlined in Scheme 1b, was challenging because of their relatively lesser solubilities in chlorinated solvents, compared with those in the X_n -Hex series. Milligram quantities of X_3 -Ph, contaminated by a phthalate impurity which most likely arises from decarboxylative side reactions, were isolated after repeated preparative TLC. Nonetheless, we proceeded to attempt the crystallization of both X_2 -Ph and X_3 -Ph.

Figure 2. Tubular representation (a/b) of the solid-state structure of X_2 -Ph. (a) A side-on view down the N–N axis of one of the PI units reveals a slight tilt with respect to the adjacent one. (b) A view down the C–C bond between the PI units reveals their near orthogonal arrangement with respect to each other. (c) A tubular and space-filling representation of the solid-state superstructure reveals that despite the geometrical complexity of X_2 -Ph, the molecules are able to adopt a tightly packed highly symmetrical arrangement.

Single crystals of X_2 -Ph suitable for X-ray diffraction, were obtained by vapor diffusion between a solution of the compound in 1:1 CH₃Cl/MeOH and a MeOH reservoir. The solid-state structure reveals that X_2 -Ph crystallizes in the tetragonal I_4/a space group (No. 88). The asymmetric unit consists of one complete PI unit which constitutes half of an X₂-Ph molecule. The C-C bond formed during the homocoupling reaction has a bond length of 1.48 Å, a value which does not differ significantly from the aryl-aryl bond length (1.51 Å) in biphenyl in its solid state.⁵² In each X2-Ph molecule, the PI units project away from the axis containing the aryl-aryl bond, such that the two PI units are tilted 97° apart (Figure 2a). The PI units are oriented in a near-orthogonal and criss-crossed manner with respect to each other with a torsional angle of approximately 89° (Figure 2b). The solvent-free superstructure is characterized by the fact that, despite their crisscross shape, the molecules of X_2 -Ph are able to pack in a surprisingly efficient manner into a unit cell that has only 21.9% void volume in a way that maximizes π - π stacking interactions between the PI units. Throughout the superstructure, pairs of X_2 -Ph molecules are packed together intimately with their vertices pointed directly at each other, while the remaining aromatic PI surfaces are satisfied by face-to-face π - π stacking with additional **X**₂-**Ph** molecules, as evidenced by the distance of 3.26 Å between the PI benzenoid planes (Figure 2c). While small, needle-like single crystals of X_3 -Ph were obtained by vapor diffusion of hexanes into a CHCl₃ solution of the compound, we were unable, however, to detect any significant diffraction on the part of these crystals.

Electrochemistry. The solid-state structure of X_2 -Ph confirms that the imide groups are located in close proximity to each other, suggesting that they may experience favorable spin-spin interactions once the compounds have been transformed into their reduced states.⁵³⁻⁵⁸ Each X_n -R

oligomer containing n PI groups is capable of accepting a total of 2n electrons. The redox behavior of X_n -Hex was probed (Figure 3) by electrochemical experiments (0.2 mM, 0.1 M TBAPF₆, 50 mV s⁻¹) in THF and referenced internally to the Fc/Fc⁺ couple. The accessible half-

Figure 3. Cyclic voltammograms (0.2 mM, THF, 0.1 M TBAPF₆, 50 mV s⁻¹) of **PI-Hex**, **X₂-Hex**, **X₃-Hex** and **X₄-Hex**, from top to bottom. Ferrocene was used as an internal standard and the labeled peak voltages were calibrated against the Fc/Fc^+ couple.

wave reduction potentials are listed in Table 1. In the cyclic voltammograms (CV) obtained from a solution of **X₂-Hex** in THF, four distinct processes were observed. These processes present themselves as two pairs of one-electron reductions, with the first and second one-electron reduction waves ($E_{1/2}^{1} = -1.35 \text{ V}$, $E_{1/2}^{2} = -1.59 \text{ V}$) corresponding to the formation of **X₂-Hex⁻** and **X₂-Hex²⁽⁻⁾**, respectively. The observed splitting is attributed to the Coulombic interactions that come into play when a second electron is introduced into the molecules. The initial reduction occurs at a slightly more positive potential compared to that $(E_{1/2}^{1} = -1.38 \text{ V})$ of **PI-Hex**, an observation which suggests that there is no significant conjugative interactions between the individual PI units. The second pair of one-electron reduction waves $(E_{1/2}^{3} = -2.13 \text{ V}, E_{1/2}^{4} = -2.13 \text{ V})$

$E_{\frac{1}{2}}$ / V	$E_{\frac{1}{2}}^{2}$ / V	$E_{\frac{1}{2}^{3}}/\mathrm{V}$	$E_{\frac{1}{2}}^{4}/\mathrm{V}$	$E_{\frac{1}{2}}^{5}$ / V	$E_{\frac{1}{2}}^{6}$ / V
-1.38	-2.05				
-1.35	-1.59	-2.13	-2.30		
-1.36	-1.44	-1.77	-2.00	-2.17	-2.24
-1.38^{b}	-1.60	-1.87	-2.17	-2.29^{b}	
		$E_{1/2}^{1}/V$ $E_{1/2}^{2}/V$ -1.38 -2.05 -1.35 -1.59 -1.36 -1.44 -1.38 ^b -1.60	$E_{1/2}^{1}/V$ $E_{1/2}^{2}/V$ $E_{1/2}^{3}/V$ -1.38 -2.05 -1.35 -1.59 -2.13 -1.36 -1.44 -1.77 -1.38 ^b -1.60 -1.87	$E_{1/2}^{-1}/V$ $E_{1/2}^{-2}/V$ $E_{1/2}^{-3}/V$ $E_{1/2}^{-4}/V$ -1.38 -2.05 -1.35 -1.59 -2.13 -2.30 -1.36 -1.44 -1.77 -2.00 -1.38 ^b -1.60 -1.87 -2.17	$E_{1/2}^{1/V}$ $E_{1/2}^{2/V}$ $E_{1/2}^{3/V}$ $E_{1/2}^{4/V}$ $E_{1/2}^{5/V}$ -1.38 -2.05 -1.35 -1.59 -2.13 -2.30 -1.36 -1.44 -1.77 -2.00 -2.17 -1.38 ^b -1.60 -1.87 -2.17 -2.29 ^b

Table 1. Electrochemical Data for PI-Hex and Xn-R^a

^{*a*} Halfwave potential values are given vs Fc/Fc⁺. ^{*b*} Multielectron process.

2.30 V), which are associated with the formation of X_2 -Hex³⁻ and X_2 -Hex⁴⁻, respectively, are shifted toward more negative potentials than the second reduction ($E_{1/2}^2 = -2.05$ V) of PI-Hex. The overall splitting of the reductions into four distinct processes suggests that, in the symmetrically identical PI redox centers, the imide units in X_2 -Hex are located in close enough proximity to each other to impose repulsive Coulombic interactions which shift subsequent reductions toward more negative potentials. Cyclic voltammetry also confirmed that X_3 -Hex undergoes six distinct reversible one-electron reductions to the hexa-anion state X_3 -Hex⁶⁻. For X_4 -Hex, 8-electron reversible reductions are detected, which proceed from the neutral state to the octa-anion state. Notably, the first two electron reduction waves in X_4 -Hex are overlapping, indicating that these two electrons communicate with each other very weakly, most likely because they are injected into the two terminal PI units to avoid unfavorable Coulombic repulsions. The subsequent two single-electron processes are most likely associated with the sequential reductions of the two "inner" PI units of X_4 -Hex. All of the initial reduction potentials

are essentially independent of the oligomer length, thus excluding any significant conjugation effect. In order to obtain further information on the electronic states for the reduced species of X_n -Hex, we measured the optical absorption changes of X_n -Hex during the course of reduction from neutral to anionic states by performing chemical reduction titration experiments.

UV-Vis-NIR Absorption Spectroscopy. While the monoreduced radical anion X_2 -Hex⁻ could be generated by chemical reduction with 1 equiv of cobaltocene (CoCp₂, $E_{1/2} = -1.33$ V vs Fc) (Figure S2 and S3), it was necessary to employ the more strongly reducing decamethylcobaltocene (CoCp*₂, $E_{1/2} = -1.91$ V) to obtain X₂-Hex²⁽⁻⁾. Accordingly, a solution of CoCp*2 was added into a 0.4 mM solution of X2-Hex in DMF in order to obtain the singly and doubly reduced states of the compound and their UV-Vis-NIR spectra (Figure 4) were recorded. The wavelengths and molar absorptivities of major bands are summarized in Table 2. The UV-Vis-NIR spectrum of the radical anion X_2 -Hex⁻ reveals two absorption bands, centered at 651 and 716 nm, corresponding^{39,59-60} closely to the wavelengths of the absorption bands for PI-Hex⁻. In addition to these two bands, however, the spectrum also displays a new band at 790 nm with a molar absorptivity similar to the one present at 716 nm. The new band might be assigned to the intervalence charge transfer band (IVCT, Figure 4), characteristic of mixed-valence compounds. Addition of a second equivalent of $CoCp_2^*$ to the solution yielded X₂-Hex²⁽⁻⁾ quantitatively, as indicated by the disappearance of the IVCT band. The absorption spectrum of the doubly reduced state, which resembles PI-Hex⁻ rather than X₂-Hex⁻, has an intense band centered at 730 nm. Unsurprisingly, addition of excess equivalents of $CoCp_{2}^{*}$ to the solution did not produce any significant changes in the UV-Vis-NIR spectra, confirming that the further reduced X_2 -Hex species could not be generated because the potentials required to access them

Figure 4. (a) UV-Vis-NIR absorption spectra (DMF, 296 K) of **PI-Hex**⁻ and **X**_n-Hex^{n(•-)} (n = 2-4), which were generated by chemical reduction of **X**_n-Hex with n equiv of CoCp*₂, respectively.

are more negative than the reduction potential of CoCp_{2}^{*} . The monoreduced X_{3} -Hex⁻ anion displays a similar IVCT band at ca. 790 nm, corresponding to the optically induced CT between the terminal PI and the central one. Notably, an additional lower energy and weaker transition is observed at around 955 nm (IVCT', Figure 4), which is assigned to the CT interaction between the two terminal PIs. This assignment is further corroborated by the disappearance of the 955 nm band upon addition of the second equivalent of CoCp_{2}^{*} to reduce both terminal PIs. The spectral features of X_{3} -Hex²⁽⁻⁾ and X_{3} -Hex³⁽⁻⁾ resemble closely those of X_{2} -Hex⁻ and X_{2} -Hex²⁽⁻⁾,

respectively. Similar trends in spectral changes are observed upon sequential reduction of X_4 -Hex, where X_4 -Hex⁴⁽⁻⁾ is relatively similar to X_2 -Hex²⁽⁻⁾ and X_3 -Hex³⁽⁻⁾.

Compound	$\lambda_{\rm max}$ / nm	$\epsilon / 10^3 { m M}^{-1} { m cm}^{-1}$
PI-Hex	320	2.6
PI-Hex [⊷]	650	7.1
	716	30.9
X2-Hex	327	4.2
X2-Hex	650	5.1
	716	10.4
	790	8.6
X2-Hex ^{2(•-)}	730	29.3

Table 2. UV-Vis Absorption Properties of PI-Hex and X2-Hex as well as their Reduced States.

Computational Results. DFT (B3LYP/6-31G*) calculations for **PI-Me**, **X**₂-**Me**, **X**₃-**Me** and **X**₄-**Me** (in which hexyl groups are simplified to -CH₃) provided insight into their conformations and energetics. In the oligomers, the PI units are severely twisted relative to one another, which is consistent with the single-crystal structure; φ , the torsional angle between the planes containing each PI units, varies from 62° to 90° depending on the redox and electron spin states (Figures S4 and S5, Tables S1 and S2).

Frontier molecular orbitals for **PI-Me**, **X₂-Me**, **X₃-Me** and **X₄-Me** were also computed (DFT, B3LYP/6-31G*). The LUMO and LUMO+1 of the **X₂-Me** are bonding and antibonding combinations, respectively, of two PI LUMOs (Figure S4). The degrees of electronic communication in the PI oligomers can be quantified by considering the energy splitting between

the LUMO and LUMO+1 orbitals of the neutral states.⁶¹ The computed splitting values, which corresponds to twice the electronic coupling (V) according to energy-splitting-in-dimer (ESD) method combined with Koopmans' Theory (KT),⁶² was 476, 532, 387 cm⁻¹ (gas phase, B3LYP/61G*) for **X₂-Me**, **X₃-Me** and **X₄-Me**, respectively. Thus, the corresponding computed electronic coupling between the PI units is significantly smaller than the reorganization energy associated with the rylene diimide anion formation (around 0.28 eV or 2300 cm⁻¹ in gas phase). Therefore, these compounds are expected to localize the charge on a single PI unit (Robin-Day class II mixed valence⁶³ rather than allowing full electron delocalization. The small computed electronic coupling in the oligomeric systems, which agrees well with experimental electrochemical results showing very little anodic shift of their first reduction potential compared to that of monomeric reference compound, can be rationalized by the nearly orthogonal conformation between the PI units and the presence of a nodal plane in the C-C bond linking them. In order to further corroborate our interpretation on the electronic distribution in these compounds we performed EPR/ENDOR measurements.

EPR/ENDOR Spectroscopy. EPR and ENDOR spectroscopies were performed on the chemically generated mono- and di-reduced states of X_2 -Hex and compared with the EPR spectrum of **PI-Hex**⁻ with particular attention being paid to understanding spin localization or delocalization with respect to each PI unit in the mono-anion and the presence of higher spin multiplicities in the more highly reduced states. The solution state cw-EPR spectra of **PI-Hex**⁻, X_2 -Hex⁻, X_3 -Hex⁻, and X_4 -Hex⁻, respectively, are shown in Figure 5a. Spectral simulation of **PI-Hex**⁻, overlaid in red, provides the hyperfine coupling values presented in Table 3, which agree well with those reported in the literature.⁶⁴ Although the spectrum of X_2 -Hex⁻ shows the

PI-Hex*-

X₂-Hex⁻⁻

X₃-Hex*-

X₄-Hex[•]

PI-Hex

Ż

339.6

Figure 5. (a) Solution (0.4 mM, DMF, 250 K) X-band EPR spectra of PI-Hex⁻, X₂-Hex⁻, X₃-Hex⁻, and X₄-Hex⁻. (b) Solution (0.4 mM, DMF, 250 K) cw-ENDOR spectra of PI-Hex⁻, X₂-Hex⁻, and X₃-Hex⁻. The corresponding spectral simulation are overlaid in red.

same spectral width as **PI-Hex**⁻, the lines are considerably broadened, an observation which makes the simulation of both the nitrogen and hydrogen hyperfine couplings difficult. The cw-EPR spectra of X_3 -Hex⁻, and X_4 -Hex⁻ also show the same spectral width as **PI-Hex⁻** but are broadened further as compared to X_2 -Hex⁻. This line broadening observed in X_2 -Hex⁻, X_3 -Hex⁻, and X_4 -Hex⁻ is likely caused by the slowing down of tumbling rate associated with increasing molecular size.⁶⁵⁻⁶⁶

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Table 3. EPR/ENDOR Spectroscopic Data for the Radical Monoanions of PI-Hex and X₂-Hex

Compound	<i>a</i> _N / MHz	a _{Hcore} / MHz	<i>a</i> _H (CH ₂) / MHz		
PI-Hex⁺-	3.35 (x2)	1.80 (x2)	0.73 (x4)		
X₂-Hex [←]	-	1.82	0.70		
The number of equivalent nuclei sharing the hfcc values are given in the parentheses.					

In order to extract the hyperfine couplings, continuous wave ENDOR spectroscopy was performed on PI-Hex⁻, X₂-Hex⁻, and X₃-Hex⁻, and electron spin echo envelope modulation $(ESEEM)^{67}$ spectroscopy was performed on both **PI-Hex**⁻ and **X**₂-**Hex**⁻. The ENDOR spectrum of **PI-Hex**⁻ shows a pair of proton resonances that were simulated with isotropic hyperfine couplings of 1.82 and 0.70 MHz (Figure 5b). These values were used in the simulation of the cw-EPR spectrum. The ENDOR spectra of X_2 -Hex⁻, and X_3 -Hex⁻ both show splitting patterns similar to those found in **PI-Hex**⁻, an observation which suggests that the unpaired electron spin density is localized on a single PI unit in the dimer. If the electron was delocalized or hopping rapidly among multiple PI units, the proton hyperfine coupling would be expected to decrease linearly with the number of units following the McConnell relationship.⁶⁸⁻⁶⁹ The cw-ENDOR spectrum of X_4 -Hex⁻ was barely observed above the noise level and is shown in Figure S6. As additional verification of spin localization, 3-pulse ESEEM was performed on both X_2 -Hex⁻ and **PI-Hex**⁻, Figure S7. The two spectra show no differences, a result which confirms that both the number of equivalent imide nitrogens and the magnitude of their hyperfine coupling are the same.

Figure 6 shows the W-band (94 GHz) EPR spectra recorded in frozen solution at 120 K of the radical mono-anions X_2 -Hex⁻ and PI-Hex⁻, the radical dianion X_2 -Hex²⁽⁻⁾, the radical trianion X_3 -Hex³⁽⁻⁾ and the radical tetraanion X_4 -Hex⁴⁽⁻⁾, with their corresponding simulation overlaid in red. Simulation of X_2 -Hex⁻ and PI-Hex⁻ provides the same g-tensor, g = [2.00485, 2.00485, 2.00485, 2.00213], which is further evidence that suggests X_2 -Hex⁻ and PI-Hex⁻ are magnetically equivalent. Additional reduction of X_2 -Hex⁻ to X_2 -Hex²⁽⁻⁾, leads to the appearance of an EPR signal characteristic of a triplet spin state, the spectrum also shows a monoreduced impurity in

Figure 6. W-band EPR spectra of frozen solutions (0.4 mM, DMF, 120 K) of PI-Hex⁻, X_2 -Hex⁻, X_2 -Hex³⁽⁻⁾, X_3 -Hex³⁽⁻⁾ and X_4 -Hex⁴⁽⁻⁾.

the central spectral region. Simulation of the two interacting PI units was achieved by rotating the g-tensor of one PI unit by 80° about the y-axis relative to the other and using a dipole-dipole coupling of 143 MHz collinear with the y-axes of the g-tensors. The observed dipole-dipole coupling allows an estimation of the mean distance between the interacting spins in X_2 -Hex²⁽⁻⁾ by the point-dipole approach,⁷⁰ which is calculated to be 7.1 Å. The structural details obtained from fitting the W-band EPR spectrum of X_2 -Hex²⁽⁻⁾ agree well with the solid-state structure (Figure 2b) of X_2 -Ph and shows that the each electron is essentially localized within one PI unit.

Figure 7. Schematic diagram for possible dipole-dipole couplings in X_4 -Hex^{4(•-)}. The W-band EPR spectra of X_3 -Hex^{3(•-)} and X_4 -Hex^{4(•-)} also show broad features which are consistent with ferromagnetic spin-spin interactions (Figure 6). Due to the complexity of the magnetic interactions in X_3 -Hex^{3(•-)} and X_4 -Hex^{4(•-)} fitting of the W-band spectrum is challenging; however, the magnetic interactions can be understood by considering a simple model and the cw-EPR data collected at X-band. The X-band cw-EPR spectrum of the radical

dianion X_3 -Hex²⁽⁻⁻⁾ and its simulation are shown in Figure S8. On top of the large mono-reduced impurity, the dianion is observed to have a dipole-dipole splitting of 55 MHz, which corresponds to a distance of 9.8 Å, which is not unreasonable for the distance between the two terminal PI units. Referring to Figure 7, from this measurement we obtain D_{13} , the dipole-dipole coupling between PI 1 and 3, and from the W-band cw-EPR of X_2 -Hex²⁽⁻⁻⁾ we obtain the nearest neighbor dipole-dipole coupling, D_{12} .

The X-band cw-EPR spectra of X_4 -Hex⁴⁽⁻⁾ shown in Figure 8 was collected as a function of temperature from 5 to 60 K. The amplitude of the broad features which correspond to the dipole-dipole coupling D_{12} decrease with decreasing temperature, which occurs concurrently with an

Figure 8. Variable temperature X-band EPR spectra of frozen DMF solution of X₄-Hex⁴⁽⁻⁾.

increase in the amplitude of the narrow, D_{13} , features. As the temperature is lowered below about 20 K, adjacent spins in X_n -Hexⁿ⁽⁻⁾ tend to pair up, turning off the nearest neighbor dipole-dipole

coupling, while the longer range (D_{13}) spin-spin interactions increasingly apparent in the overall cw-EPR spectra.

CONCLUSIONS

In summary, we have reported the synthesis and isolation of three X-shaped oligomeric pyromellitimides that are readily soluble in organic solvents. The dimeric compound X_2 -Ph was found by X-ray crystallography to crystallize in an aesthetically pleasing and highly packed superstructure that highlights the proximity of the two pyromellitimide units to each other within the molecule. Cyclic voltammetry reveals that the enforced interaction between imide units leads to three, five or seven individually accessible redox states. UV-Vis-NIR and EPR/ENDOR spectroscopic experiments performed on the chemically-generated singly-reduced state of X₂-**Hex**, shows localization of the unpaired electron on an individual pyromellitimide unit. EPR spectroscopy also demonstrates antiferromagnetic spin-spin interactions for the radical anions X_2 -Hex²⁽⁻⁾, X_3 -Hex³⁽⁻⁾ and X_4 -Hex⁴⁽⁻⁾ at temperatures < ~20K resulting in low spin ground states, while low-lying thermally accessible high-spin ($S > \frac{1}{2}$) states are populated at temperatures $> \sim 20$ K. This research shows that decreasing the electronic coupling between the unpaired spins on adjacent PI molecules by fixing their π systems in a nearly orthogonal geometry results in the ability to maintain high spin multiplicity spin states in these oligomers, which may prove useful in developing molecular magnets and quantum information systems.

EXPERIMENTAL SECTION

Synthetic Methods. Unless otherwise stated, compounds and solvents were purchased from commercial vendors and were used as supplied without further purification. Copper bronze was

activated by a 2% I₂ solution in Me₂CO immediately prior to use. Nuclear magnetic resonance (NMR) spectra were recorded at 298 K on a Bruker Avance III 500 spectrometer, with a working frequency of 500 MHz for ¹H and 125 MHz for ¹³C. Chemical shifts are listed in ppm on the δ scale and coupling constants are recorded in Hertz (Hz). Deuterated solvents for NMR spectroscopic analyses were used as received. Chemical shifts are reported in δ values relative to the signals corresponding to the residual non-deuterated solvents (CD₃COCD₃: $\delta_{\rm H}$ 2.05 ppm, $\delta_{\rm C}$ 29.84 ppm; CDCl₃: $\delta_{\rm H}$ 7.26 ppm, $\delta_{\rm C}$ 77.23 ppm; CD₃COCD₃: $\delta_{\rm H}$ 2.50 ppm, $\delta_{\rm C}$ 39.57 ppm). Lowand high-resolution mass spectra were measured on a Bruker Autoflex III MALDI-TOF using 2,5-dihydroxybenzoic acid as the matrix. **Synthetic Procedures.** The syntheses of the **X_n-R** compounds described in this research are

Synthetic Procedures. The syntheses of the X_n -R compounds described in this research are described in detail below. Detailed procedures for the syntheses of 2-R and 1-R precursor compounds are provided in the Supporting Information.

X₂-Hex: A mixture of **1-Hex** (100 mg, 216 μmol), activated copper bronze (100 mg), and *N*-methyl-2-pyrrolidone (5 mL) was heated in an N₂ atmosphere at 150 °C for 3.5 h. After cooling to room temp, the reaction mixture was diluted with EtOAc (30 mL) and washed with brine (3 × 30 mL). The combined organic layers were dried (MgSO₄), collected by filtration, and evaporated under reduced pressure. The residue was purified by preparative TLC (2:3 Hexanes/CH₂Cl₂ (v/v)) to yield **X₂-Hex** as a beige solid (25 mg, 30%) as well as the reduction byproduct **PI-Hex** as a white solid (31 mg, 37%). Spectroscopic characterization of **X₂-Hex**: ¹H NMR (CDCl₃, 500 MHz, 298 K): $\delta_{\rm H} = 8.37$ (s, 2H), 3.59 (t, *J* = 7.3 Hz, 8H), 1.58 (p, *J* = 7.3 Hz, 8H), 1.30–1.22 (m, 24H), 0.88–0.80 (m, 12H); ¹³C NMR (CDCl₃, 125 MHz, 298 K): $\delta_{\rm C} = 166.5$,

165.7, 136.8, 135.1, 125.2, 118.7, 38.7, 31.3, 28.3, 26.4, 22.5, 14.0; HR-MS (MALDI-TOF) Calcd for C₄₄H₅₅N₄O₈: m/z = 767.40 ($[M + H]^+$); Found: m/z = 767.35 ($[M + H]^+$).

 X_n -Hex: A mixture of 1-Hex (90 mg, 0.19 mmol), 2-Hex (50 mg, 92 μ mol), activated copper bronze (150 mg), and N-methyl-2-pyrrolidone (5 mL) was heated in an N₂ atmosphere at 150 °C for 3.5 h. After cooling to room temp, the reaction mixture was diluted with EtOAc (30 mL) and washed with brine $(3 \times 30 \text{ mL})$. The combined organic layers were dried (MgSO₄), collected by filtration, evaporated under reduced pressure, and the residue triturated with MeOH. The precipitate was purified by preparative TLC (1:3 hexanes/CH₂Cl₂ (v/v)) to yield **PI-Hex** (10.6 mg, 9.6%), X₂-Hex (21 mg, 19%), X₃-Hex (15 mg, 14%) and X₄-Hex (10 mg, 14%). Spectroscopic characterization of X₃-Hex: ¹H NMR (CDCl₃, 500 MHz, 298 K): $\delta_{\rm H} = 8.40$ (s, 2H), 3.66 (t, J = 7.4 Hz, 8H), 3.48 (t, J = 7.3 Hz, 4H), 1.64 (p, J = 7.3 Hz, 8H), 1.54–1.45 (m, 4H), 1.37–1.19 (m, 36H), 0.86 (t, J = 7.0 Hz, 12H), 0.83 (t, J = 7.0 Hz, 6H); ¹³C NMR (CDCl₃, 125 MHz, 298 K): δ_C = 166.6, 166.1, 166.0, 137.1, 135.4, 134.9, 126.1, 125.3, 118.9, 39.0, 31.6, 31.5, 28.6, 28.4, 26.7, 26.6, 22.7, 22.6, 14.2, 14.2; LR-MS (MALDI-TOF) Calcd for $C_{66}H_{80}N_6O_{12}$: m/z = 1148.58 ([M]); Found: m/z = 1148.35 ([M]). Spectroscopic characterization of **X**₄-Hex: ¹H NMR (CDCl₃, 500 MHz, 298 K): $\delta_{\rm H} = 8.40$ (s, 2H), 3.66 (t, J = 7.3 Hz, 8H), 3.53 (t, J = 7.3 Hz, 8H), 1.68-1.61 (m, 8H), 1.56-1.50 (m, 8H), 1.34-1.16 (m, 48H), 0.86 (t, J = 7.0 Hz)Hz, 12H), 0.88–0.82 (m, 24H); ¹³C NMR (CDCl₃, 125 MHz, 298 K): $\delta_{\rm C} = 166.5$, 166.2, 166.1, 165.9, 137.0, 135.4, 126.0, 38.9, 31.8, 31.6, 31.1, 28.6, 28.4, 26.7, 26.6, 22.9, 22.7, 22.7, 14.4, 14.2, 14.2; LR-MS (MALDI-TOF) Calcd for $C_{88}H_{106}N_8O_{16}$: m/z = 1531.78 ($[M + H]^+$); Found: $m/z = 1533.80 ([M + H]^+).$

X₂-Ph: A mixture of **1-Ph** (100 mg, 224 μmol), activated copper bronze (100 mg), and *N*methyl-2-pyrrolidone (5 mL) was heated in an N₂ atmosphere at 150 °C for 3.5 h. After cooling to room temp, the reaction mixture was diluted with EtOAc (30 mL) and washed with brine (3 × 30 mL). The combined organic layers were dried (MgSO₄), collected by filtration, evaporated under reduced pressure, and the residue triturated with MeOH to yield **X₂-Ph** as a brown solid (29 mg, 35.3%). ¹H NMR (CD₃COCD₃, 500 MHz, 298 K): $\delta_{\rm H} = 8.55$ (s, 2H), 7.58–7.40 (m, 20H); ¹³C NMR (CD₃SOCD₃, 125 MHz, 298 K): $\delta_{\rm C} = 165.2$, 164.6, 136.6, 134.8, 131.1, 129.1, 128.6, 127.1, 125.7, 118.9; HR-MS (MALDI-TOF) Calcd for C₄₄H₂₃N₄O₈: *m/z* = 735.15 ([*M* + H]⁺); Found: *m/z* = 735.12 ([*M* + H]⁺).

X₃-Ph: A mixture of **1-Ph** (106 mg, 237 μ mol), **2-Ph** (75 mg, 0.14 mmol), activated copper bronze (300 mg), and *N*-methyl-2-pyrrolidone (5 mL) was heated in an N₂ atmosphere at 150 °C for 3.5 h. After cooling to room temp, the reaction mixture was diluted with EtOAc (30 mL) and washed three times with brine (3 × 30 mL). The combined organic layers were dried (MgSO₄), collected by filtration, evaporated under reduced pressure, and the solids triturated with MeOH. The residue was purified by preparative TLC (1:3 hexanes/CH₂Cl₂ (v/v)) to yield **X₃-Ph** as a brown solid (3.8 mg, 35.3%) containing an impurity which could not be separated from the title compound. The byproduct is believed to be a phthalate produced by undesired decarboxylation during the course of the reaction. ¹H NMR (CD₃COCD₃, 500 MHz, 298 K): ppm = 8.58 (s, 2H), 7.55–7.33 (m, 30H).

X-Ray Crystallography. X-Ray crystal data were collected on a Bruker Kappa diffractometer equipped with a CuK_{α} sealed-tube source and an APEX II CCD detector. Intensity data were obtained using ω and φ scans spanning at least a hemisphere of reciprocal space for all structures

(data were integrated using SAINT). Absorption effects were corrected on the basis of multiple equivalent reflections (SADABS). Structures were solved by direct methods(SHELXS)⁷¹ and refined by full-matrix least-squares against F2 (SHELXL).⁷¹ The structures were solved and refined using Olex2. The hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealized geometries. Crystallographic images were produced using UCSF Chimera.⁷² Atom-to-atom distances and torsional angles were measured employing Mercury.⁷³

Crystallization Procedure and Data. A 0.5-mL solution of **X**₂-**Ph** (1 mg) was dissolved in CHCl₃/MeOH (1:1 (v/v)) and passed through a 0.45 μ PTFE syringe filter into a crystallization tube. This tube was placed in a 20-mL scintillation vial which contained MeOH (3 mL). After several weeks, colorless crystals were collected for single crystal X-ray crystallography. **X**₂-**Ph**: C₄₄H₂₂N₄O₈; colorless prism, 0.132 × 0.053 × 0.045 mm³; tetragonal, space group *I*4₁/a; *a* = 15.469(2), *b* = 15.469(2), *c* = 34.551(5) Å; $\alpha = \beta = \gamma = 90^{\circ}$; *V* = 8268 Å³; *Z* = 8; $\rho_{calcd} = 1.180$ g cm⁻³; $2\theta_{max} = 50.497^{\circ}$; *T* = 100 K; 9253 reflections collected, 2142 independent, 253 parameters; $\mu = 0.1686$ mm⁻¹; *R*₁ = 0.0694 [*I* > 2 σ (*I*)], *wR*₂ = 0.1715 (all data); CCDC deposition number 1402122.

Electrochemistry. Cyclic voltammetry (CV) experiments were performed on a Gamry Reference 600 instrument interfaced to a PC using a glassy carbon working electrode (0.071 cm²). The electrode surface was polished routinely with 0.05 μ m² alumina/H₂O slurry on a felt surface immediately before use. The counter electrode was a Pt coil and the reference electrode was an AgCl-coated Ag wire. The concentrations of the samples were 1 mM in 0.1 M electrolyte

 solution (TBAPF₆ in THF or DMF). Electrochemical experiments were conducted on solutions before and after addition of a ferrocene internal standard.

UV-Vis-NIR. The radical anionic and dianionic states of the compounds investigated were generated by addition of 1 or 2 equiv, respectively, of decamethylcobaltocene (CoCp*₂) into DMF solutions under an Ar atmosphere. UV-Vis-NIR spectra were recorded on a Shimadzu UV-1800 instrument.

Computational Details. Model structures for the X_n -R compounds, where R are methyl substituents instead of hexyl groups , were optimized with DFT calculations by using B3LYP functional,⁷⁴ which combines Becke's three parameter hybrid-exchange functional⁷⁵ with the Lee–Yang–Parr correlation functional,⁷⁶ and the 6–31G* basis set. Frequency calculations on the optimized geometries indicated no imaginary frequencies. Note that unrestricted UB3LYP functional calculation on the anionic states predicts fully delocalized structures for all of compounds and localization was not achieved by the inclusion of solvation effects with polarizable continuum model (PCM) approach.⁷⁷ This over-delocalization impeded us to perform any meaningful TD-DFT calculations to support the assignment of UV-Vis-NIR absorption bands.

EPR Spectroscopy. All EPR sample preparations were performed under an argon atmosphere. The concentrations of the samples were 0.4 mM in DMF as verified by UV-Vis-NIR absorption spectra. Samples were loaded into quartz 1.4 mm tubes and sealed with a clear ridged UV doming epoxy (IllumaBond 60-7160RCL) and used immediately after preparation. Solution state continuous wave EPR and ENDOR measurements at X-band (9.5 GHz) were performed with a Bruker Elexsys E680-X/W EPR spectrometer, equipped with an EN801 ENDOR resonator; solid state CW-EPR and Pulsed EPR measurements at X-band were performed using a split ring resonator (ER4118X-MS5); and W-band measurements utilized a cylindrical resonator (EN-680-1021H). ENDOR experiments were performed using the DICE ENDOR accessory and an ENI A-500 RF power amplifier. A 1 kW TWT amplifier (Applied Systems Engineering 117X) was employed to generate high-power microwave pulses. 3-pulse ESEEM experiments were collected using the standard $\pi/2 - \tau - \pi/2 - T - \pi/2$ pulse sequence, where pulses of turning angle $\pi/2$ were 16 ns in length, τ was fixed at 200 ns, and T was varied in steps of 16 ns. The EPR and ENDOR spectra were fit in MATLAB® (The MathWorks Inc., Natick MA) using Easyspin v5.0.16.⁷⁸

ASSOCIATED CONTENT

Supporting Information

Detailed synthetic procedures, crystallographic and spectroscopic (NMR, HRMS, UV-Vis-NIR, and CV) characterization for **1-R**, **1-Hex** and **1-Ph** are included within SI. Additional EPR data is also presented. This material is available free of charge via the Internet at http://pubs.acs.org. The crystallographic parameters of single crystal are deposited in the Cambridge Crystallographic Data Centre (CCDC).

AUTHOR INFORMATION

Corresponding Authors

dcao@macalester.edu, m-wasielewski@northwestern.edu, stoddart@northwestern.edu

Present Addresses

(D.C.) Chemistry Department, Macalester College, 1600 Grand Ave, St Paul, MN 55105, USA.

Notes

The authors declare no competing financial interest.

[†]Yilei Wu, Ji-Min Han, and Michael Hong contributed equally to this work.

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