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Synthesis and Study of Differentially Substituted Dibenzotetraazafulvalenes

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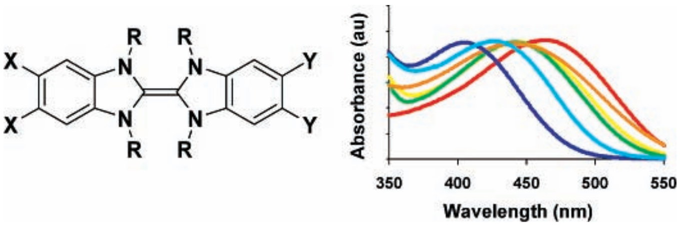
ABSTRACT



A series of functionalized dibenzotetraazafulvalenes have been synthesized and characterized using X-ray crystallography, UV–vis spectroscopy, and cyclic voltammetry. The solid-state structures, electronic properties, and redox potentials of these compounds varied in accordance with the nature of the pendant arene substituent.

The design and development of conjugated organic polymers is a rapidly expanding area of research, holding considerable promise in applications ranging from lightweight batteries to solar cells.[1] Common conjugated polymers such as polyacetylene, polythiophene, and polyaniline are structurally robust materials prepared using kinetically controlled (i.e., nonreversible) polymerization methods. With applications in self-healing electronics and reconfigurable systems in mind, we are interested in developing structurally reversible, conjugated polymers that respond to changes in externally applied stimuli.[2]

Capitalizing on the Wanzlick equilibrium[3] (i.e., the reversible dimerization of certain classes of *N*-heterocyclic carbenes), we reported[4] a series of polyenetetraamines derived from a Janus-type bis(carbene)[5] building block. While this thermally reversible polymerization formally conserved chemical unsaturation as monomer was converted to polymer, only modest bathochromic shifts in the respective UV−vis absorption spectra were observed ($\Delta\lambda_{max} = 80$ nm). This result indicated that the material was only moderately electronically delocalized, restricting utility in the aforementioned applications.

One possible source of the electronic impedance was the tetraaminoethylene groups within the dibenzotetraazafulvalene[6] (DBTF) repeat unit of the polymer backbone (see Scheme 1). While DBTFs have found utilities in many facets of chemistry, including use in electrically conductive charge-transfer complexes,[7] in the formation of organometallic complexes,[8] in the synthesis of benzimidazole derivatives,[9]

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[1] (a) Shirakawa, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 2574. (b) MacDiarmid, A. G. *Angew. Chem., Int. Ed.* **2001**, *40*, 2581. (c) Heeger, A. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 2591. (d) McCullough, R. D. *Adv. Mater.* **1998**, *10*, 93. (e) Conjugated Polymers: Theory, Synthesis, and Characterization. In *Handbook of Conducting Polymers*, 3rd ed.; Skotheim, T. A., Reynolds, J. R., Eds.; CRC Press: Boca Raton, FL, 2006.

[2] (a) Williams, K. A.; Boydston, A. J.; Bielawski, C. W. *J. R. Soc. Interface* **2007**, *4*, 359. (b) Boydston, A. J.; Williams, K. A.; Bielawski, C. W. *J. Am. Chem. Soc.* **2005**, *127*, 12496.

[3] (a) Böhm, V. P. W.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 4036. (b) Hahn, F. E.; Wittenbecher, L.; Le Van, D.; Fröhlich, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 541. (c) Liu, Y. F.; Lemal, D. M. *Tetrahedron Lett.* **2000**, *41*, 599. (d) Liu, Y.; Lindner, P. E.; Lemal, D. M. *J. Am. Chem. Soc.* **1999**, *121*, 10626. (e) Wanzlick, H. W.; Ahrens, H. *Chem. Ber.* **1964**, *97*, 2447.

[4] Kamplain, J. W.; Bielawski, C. W. *Chem. Commun.* **2006**, 1727.

[5] Khramov, D. M.; Boydston, A. J.; Bielawski, C. W. *Angew. Chem., Int. Ed.* **2006**, *45*, 6186.

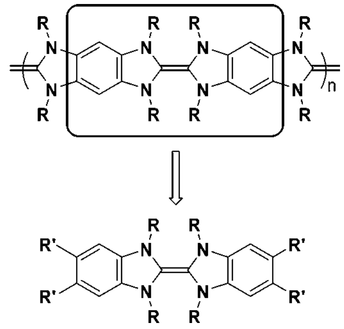
[6] Although compounds **1**−**7** are formally 1,1′,3,3′-tetraalkylbibenzimidazolinylidenes, they are also known as DBTFs by analogy to tetrathiafulvalenes; see: (a) Hahn, F. E.; Wittenbecher, L.; Kühn, M.; Lügger, T.; Frölich, R. *J. Organomet. Chem.* **2001**, *617*−*618*, 629. (b) Shi, Z.; Goulle, V.; Thummel, R. P. *Tetrahedron Lett.* **1996**, *37*, 2357.

[7] Wheland, R. C.; Gillson, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 3917.

[8] Hitchcock, P. B.; Lappert, M. F.; Terroros, P.; Wainwright, K. P. *J. Chem. Soc., Chem. Commun.* **1980**, 1180.

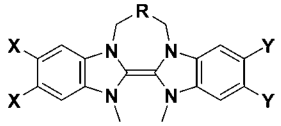
10.1021/ol702230r CCC: $37.00

Scheme 1. The Repeating Unit of the Polyenetetraamine Shown Is Effectively a Derivative of Dibenzotetraazafulvalene



and as “super electron donor” reagents,[10] less is known about their structural and electronic properties.[11] For example, DBTF **1** (see Table 1) was reported[12] to exhibit typical C−N lengths (∼1.43 Å) and a 14° torsion angle about the enetetraamine unit; hence, electronic delocalization between the arene rings appeared to be minimal in this compound.

Table 1. Selected Structural Data of DBTFs[a]



no.	R	X	Y	C=C[b] (Å)	CNC[c] (deg)	$\tau_{C=C}$[d] (deg)
1	2H	H	H	1.344(4)	113	14
2	2H	OMe	OMe	1.338(16)	113	7
3	2H	Br	Br	1.348(8)	116	27
4	2H	Cl	Cl	nd	nd	nd
5	$(CH_2)_2$	OMe	Br	nd	nd	nd
6	$(CH_2)_2$	OMe	OMe	nd	nd	nd
7	$(CH_2)_2$	Br	Br	1.343(10)	117	18

[a] See text for synthesis. [b] Average length of the carbon−carbon double bond. [c] Average angle of the contiguous C−N−C systems. [d] Absolute torsion angle about the enetetraamine. nd = not determined.

The primary purpose of this study was to determine the extent to which electronic communication occurs through the enetetraamine linkage. In particular, the synthesis and study of a donor−acceptor DBTF, featuring electron-donating groups on one arene ring and electron-withdrawing groups on the other, is described. For comparison, symmetrically functionalized DBTFs were also prepared. The structural, electronic, and redox properties of these compounds were evaluated using X-ray crystallography, UV−vis spectroscopy, and cyclic voltammetry, respectively.

Various symmetrically and asymmetrically functionalized DBTFs bearing electron-donating and -withdrawing groups[13] are shown in Table 1. Symmetric DBTFs **1**−**4** were synthesized using a two-step procedure. First, their respective 1-methylbenzimidazoles were alkylated with CH_3I in CH_3CN to afford the corresponding 1,3-dimethylbenzimidazolium salts. These salts were then deprotonated with NaH,[14] facilitated with a catalytic amount of KO^{t}Bu, in benzene to generate the respective benzimidazolinylidenes in situ, which ultimately dimerized to afford the desired DBTFs.[15,16]

To prepare an asymmetrically functionalized DBTF (i.e., a donor−acceptor analogue), a linker was required to ensure proper registry. DBTF **5** was synthesized by first alkylating 5,6-dimethoxy-1-methyl-benzimidazole with excess 1,4-dibromobutane in CH_3CN. The resulting salt was then treated with 4,5-dibromo-1-methylbenzimidazole to obtain the respective bisbenzimidazolium salt. Subsequent deprotonation using the protocol described above afforded the desired asymmetric DBTF. To account for effects caused by the four-carbon linker, tethered analogues **6** and **7** were synthesized in a similar fashion[17] and compared with their parent compounds **2** and **3**.

Crystals suitable for X-ray diffraction were obtained for **2**, **3**, and **7** by slow diffusion of ether into saturated THF solutions;[18] ORTEP diagrams for **2** and **3** are shown in parts A and B, respectively, of Figure 1.[19] While the lengths of the carbon−carbon double bonds were similar for each of these compounds (see Table 1), comparison of **2** and **3** revealed that the geometries about the enetetraamine units were strongly influenced by the pendant functional groups. For example, the methoxy substituents in **2** appeared to enhance *N*-pyramidalization (avg C−N−C angle = 113°). This structural arrangement effectively minimized steric interactions between opposing *N*-methyl groups and afforded a nearly planar enetetraamine moiety (abs torsion = 7°).[20]

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(9) (a) Küçükbay, H.; Çetinkaya, E.; Cetinkaya, B.; Lappert, M. F. *Synth. Commun.* **1997**, *27*, 4059. (b) Shi, Z.; Thummel, R. P. *J. Org. Chem.* **1995**, *60*, 5935.

(10) (a) Schoenebeck, F.; Murphy, J. A.; Zhou, S.-Z.; Uenoyama, Y.; Miclo, Y.; Tuttle, T. *J. Am. Chem. Soc.* **2007**, *129*, 13368. (b) Murphy, J. A.; Zhou, S.-Z.; Thomson, D. W.; Schoenebeck, F.; Mohan, M.; Park, S. R.; Tuttle, T.; Berlouis, L. E. *Angew. Chem., Int. Ed.* **2007**, *46*, 5178. (c) Murphy, J. A.; Khan, T. A.; Zhou, S.-Z.; Thomson, D. W.; Mahesh, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 1356.

(11) This is primarily due to their extreme sensitivities toward air and water. As a result, very few X-ray structures of DTBFs are known.[3b,5,12]

(12) Çetinkaya, E.; Hitchcock, P. B.; Küçükbay, H.; Lappert, M. F.; Al-Juaid, S. *J. Organomet. Chem.* **1994**, *481*, 89.

(13) 5-Nitro-1,3-dimethylbenzimidazolium bromide was found to decompose upon treatment with NaH/KO^{t}Bu.

(14) (a) Bourson, J. *Bull. Soc. Chim. Fr.* **1971**, 3541. (b) Hünig, S.; Scheutzow, D.; Schlaf, H.; Quast, H. *Liebigs Ann. Chem.* **1972**, *765*, 110.

(15) Due to the extreme sensitivities of DBTFs toward O_2 and/or H_2O, reaction mixtures were typically filtered through PTFE membranes to remove residual inorganic salts and analyzed directly.

(16) Small amounts of free benzimidazolinylidenes were observed for each of the DBTFs shown in Table 1. For an excellent, comprehensive analysis of diaminocarbene dimerizations, see: Alder, R. W.; Blake, M. E.; Chaker, L.; Harvey, J. N.; Paolini, F.; Schütz, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 5896.

(17) For related syntheses, see: (a) Ames, J. R.; Houghtaling, M. A.; Terrian, D. L.; Mitchell, T. A. *Can. J. Chem.* **1997**, *75*, 28. (b) Taton, T. A.; Chen, P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1011. (c) Shi, Z.; Thummel, R. P. *Tetrahedron Lett.* **1995**, *16*, 2741. (d) Thummel, R. P.; Goulle, V.; Chen, B. *J. Org. Chem.* **1989**, *54*, 3057. (e) Hünig, S.; Sheutzov, D.; Schlaf, H. *Justus Liebigs Ann. Chem.* **1972**, *765*, 126.

(18) All attempts to grow quality crystals for **4**−**6** were unsuccessful.

(19) The structure of **7** was found to be superficially similar to **3**; see the Supporting Information.

(20) Low torsion (15°) and avg C−N−C (116°) angles were observed[5] in a bibenzobisimidazolinylidene, another electron-rich DBTF.

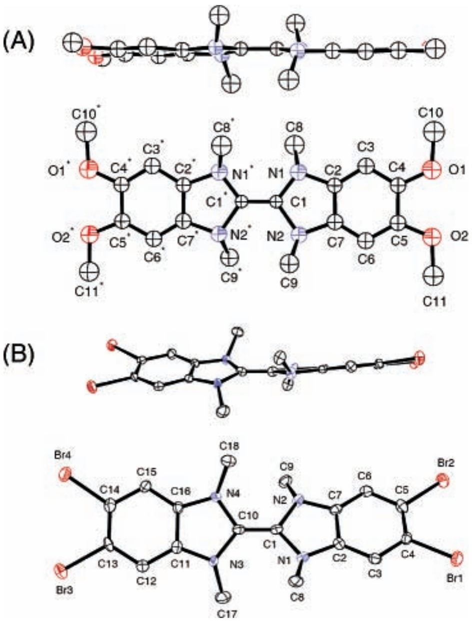


Figure 1. Two ORTEP views of **2** (A) and **3** (B). Hydrogen atoms have been removed for clarity.

In contrast, the halogen atoms in **3** appeared to decrease *N*-pyramidalization (avg C−N−C angle = 116°), which caused significant twisting about the enetetraamine (abs torsion = 27°) to avoid unfavorable steric interactions between opposing *N*-methyl groups. Although superficially similar to **3**, the enetetraamine moiety in **7** (not shown) was slightly less twisted, indicating that the four-membered linker induced partial planarization of the enetetraamine core (abs torsion angle = 18°, avg C−N−C angle = 117°).[21]

As summarized in Table 2, the pendant functional groups in DBTFs also resulted in changes in their respective UV−vis spectroscopic properties. Relative to **1** (397 nm), the λ_{max} for dimethoxy analogue **2** was bathochromically shifted to 404 nm; additional redshifting was observed for dihalo DBTFs **3** (444 nm) and **4** (441 nm). Although similar absorption characteristics were observed for bridged DBTFs **6** and **7**, their respective signals were bathochromically shifted by ca. 20 nm relative to their parent analogues, presumably due to linker-induced planarization. The donor−acceptor DBTF **5** exhibited a λ_{max} = 441 nm which was intermediate of its symmetric dimethoxy (425 nm) and dibromo (464 nm) analogues. Collectively, these results suggested that electronic delocalization through the enetetraamine moiety in the DBTFs analyzed was relatively minimal.

Table 2. Selected Spectroscopic Properties and Redox Potentials of Dibenzotetraazafulvalenes

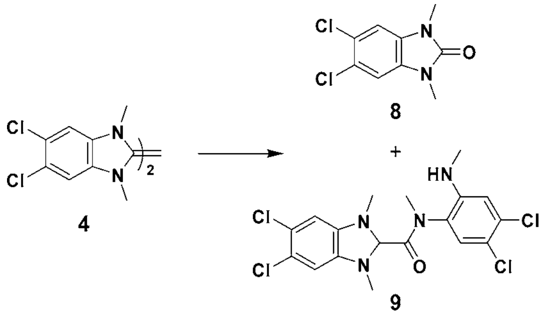
no.	λ_{max}[a] (nm)	log (ϵ)[a]	$E_{1/2}$[b] (V)	$E_{1/2}$[c] (V)
1	397	3.92	-0.90	
2	404	4.06	-1.07	
3	444	3.98	-0.73	-0.64
4	441	4.00	-0.69	
5	441	4.05	-0.93	-0.82
6	425	4.00	-1.07	
7	464	3.97	-0.76	-0.59

[a] Determined in C_6D_6 at 23 °C. [b] Values reported are relative to SCE. Redox potentials were determined in CH_3CN at 23 °C using 0.1 M tetrabuylammonium hexafluorophosphate as electrolyte versus a Pt-polypyrrole electrode externally referenced to ferrocene/ferrocenium at a scan rate = 100 mV/s. [c] For compounds **3**, **5**, and **7**, a second redox process was observed at the potential indicated.

Finally, the redox potentials ($E_{1/2}$) of **1**−**7** were evaluated using cyclic voltammetry.[22] As summarized in Table 2, not only was a relatively broad range of $E_{1/2}$ observed, but these values correlated with the electron-donating or -withdrawing nature of peripheral substituents on the respective DBTFs.[23] For example, **2**, which possessed pendant methoxy groups, exhibited the highest $E_{1/2}$ at −1.07 V versus SCE whereas chloro bearing DBTF **4** exhibited the lowest at −0.69 V. The $E_{1/2}$ of parent hydrido DBTF **1** was intermediate of these values (−0.90 V) as was the donor−acceptor DBTF **5** (−0.93 V). The four-carbon linker in **6** (−1.07 V) and **7** (−0.76 V) appeared to have only a minor effect on $E_{1/2}$ when compared to their parent analogues (**2** and **3**, respectively). Collectively, the following trend in $E_{1/2}$ was observed (pendant substituents are shown in parentheses): **2** (OMe) ∼ **6** (OMe) > **5** (OMe, Br) ∼ **1** (H) > **7** (Br) ∼ **3** (Br) > **4** (Cl).

The observed differences in electron densities manifested in unique chemical reactivities. Although enetetraamines are known[24] to instantly oxidize to their respective cyclic ureas upon exposure to ambient oxygen, a much slower reaction was observed with DBTF **4**,[25] which features pendant chlorine groups and exhibits a relatively low oxidation potential. As shown in Scheme 2, exposure of a benzene solution of **4** to ambient atmosphere afforded urea **8** as well

Scheme 2. Exposure of DBTF **4** to Air Afforded Urea **8** and Hydrolysis Product **9** as a 4:1 Mixture



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[21] The solid-state structures of DBTFs **1**−**3** and **7** may also be influenced by crystal packing forces.

[22] Although the redox processes of DBTFs **1**−**7** appeared to be reversible, solutions of these compounds were found to decompose in the presence of electrolyte. The decomposition process may occur via their free NHCs;[16] see: Ramnial, T.; McKenzie, I.; Gorodetsky, B.; Tsang, E. M. W.; Clyburne, J. A. C. *Chem. Commun.* **2004**, 1054.

[23] For DBTFs **3**, **5**, and **7**, two $E_{1/2}$ were observed (see Table 2).

[24] Winberg, H. E.; Downing, J. R.; Coffman, D. D. *J. Am. Chem. Soc.* **1965**, *87*, 2054.

as a novel hydrolysis product (**9**) as a 4:1 mixture of over the course of 24 h (73% isolated yield). The ORTEP diagram shown in Figure 2 reveals that the solid-state structure of **9** adopted an s-trans conformation about the amide linkage. This observation may be rationalized by the intramolecular distance of 3.98 Å found between the offset centroids of the phenyl groups, indicative of a $\pi-\pi$ interaction.[26] Regardless, the relatively slow rate of this reaction suggested that electron-deficient enetetraamines are more robust toward O_2 than their electron-rich analogues.

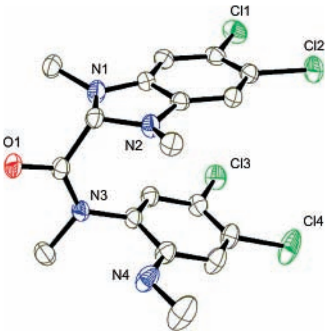

Figure 2. ORTEP view of **9**. Hydrogen atoms and solvent molecules have been removed for clarity.

In summary, a series of dibenzotetraazafulvalenes possessing a range of electron-donating and electron-withdrawing substituents were synthesized. Although X-ray crystallography and UV−vis spectroscopy suggested that electronic communication between these peripheral groups was relatively minimal, cyclic voltammetry revealed that the redox potentials of these compounds were tunable. Collectively, these results should help guide the development of new enetetraamine-based materials for electronic applications as well as new reagents for organic and organometallic synthesis.

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Supporting Information Available: Experimental procedures and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) Similar results were observed with DBTF **3**. Chemiluminescense was not visually observed in these reactions.

(26) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525.