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Remarkable Structure Deformation in Phenothiazine Trimer Radical Cation

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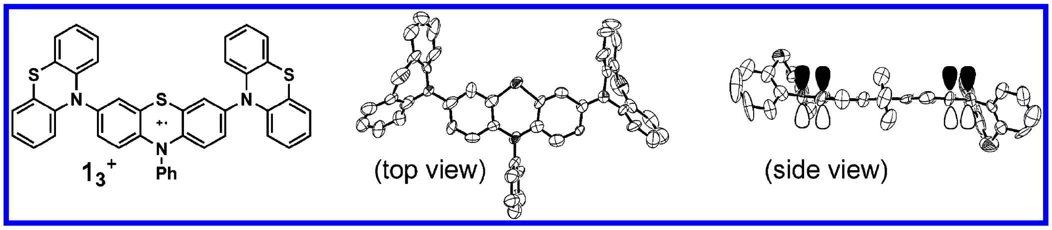
ABSTRACT



A trimeric phenothiazine and its radical cation were prepared, and their structures were elucidated. In contrast to a largely twisted structure in the neutral species, the radical cation had a unique structure deformation that allowed charge-transfer-type conjugation from the outer phenothiazine rings to the central phenothiazine radical cation.

Delocalization and localization of electrons of redox states in oligomers and dendrimers are important subjects in materials science.[1,2] Many donor- and acceptor-based molecular assemblies have been synthesized, and in some cases their redox states have been well characterized using spectroscopic methods such as UV−vis, EPR, and NMR for diamagnetic species.[1−5] Few studies, however, have provided clear insight into electron (de)localization in relation to structure terms for redox states of molecular assembly systems.[6,7] In connection with our previous studies of phenothiazine radical cations,[5a−c] we have been interested in those of higher oligomers. We report that phenothiazine trimer radical cation $\mathbf{1_3}^+$ reveals remarkable structure deformation showing a new charge transfer (CT) band in the visible region.

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(1) (a) Müllen, K., Wegner, G., Eds. *Electronic Materials: The Oligomer Approach*; Wiley-VCH: New York, 1998. (b) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendrimers and Dendorons*; Wiley-VCH: New York, 2001.

(2) For electronic interaction: (a) Nelsen, S. F. *Chem. Eur. J.* **2000**, *6*, 581−588. (b) Nelsen, S. F.; Ismagilov, R. F.; Trieber, D. A., II. *Science* **1997**, *278*, 846−849. (c) Lambert, C. L.; Nöll, G. *J. Am. Chem. Soc*. **1999**, *121*, 8434−8442.

(3) Geometrical change during oxidation of amino-olefines and -arenes has been discussed in terms of oxidation potentials: (a) Fritsch, J. M.; Weingarten, H.; Wilson, J. D. *J. Am. Chem. Soc.* **1970**, *92*, 4038−4046. (b) Nelsen, S. F.; Clennan, E. L.; Echegoyan, L.; Grezzo, L. A. *J. Org. Chem*. **1978**, *43*, 2621−2628.

(4) For oligoanilines: (a) Blackstock, S. C.; Selby, T. D. In *Magnetic Properties of Organic Materials*; Lahti, P., Ed.; Marcel Dekker: New York, 1999; pp 165−178. (b) Ito, A.; Ino, H.; Tanaka, K.; Kanemoto, K.; Tato, T. *J. Org. Chem*. **2002**, *67*, 491−498.

(5) For oligophenothiazines: (a) Okada, K. In *Molecular Magnetism*; Itoh, K., Kinoshita, M., Eds.; Kodansha-Gordon and Breach: Tokyo, 2000; pp 264−277. (b) Okada, K.; Imakura, T.; Oda, M.; Murai, H.; Baumgarten, M. *J. Am. Chem. Soc*. **1996**, *118*, 3047−3048. (c) Okada, K.; Imakura, T.; Oda, M.; Kajiwara, A.; Kamachi, M.; Sato, K.; Shiomi, D.; Takui, T.; Itoh, K.; Gherghel, L.; Baumgarten, M. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1059−1060. (d) Sun, D.; Rosokha, S. V.; Kochi, J. K. *J. Am. Chem. Soc*. **2004**, *126*, 1388−1401. (e) Krämer, C. S.; Zeitler, K.; Müller, T. J. J. *Tetrahedron Lett*. **2001**, *42*, 8619−8624. (f) Tsujino, Y. *Tetrahedron Lett*. **1968**, 2545−2550. (g) Diudea, M. V. *Tetrahedron Lett*. **1982**, *23*, 1367−1370.

(6) X-ray structure analyses for lower oligomer or dendrimer charged or spin systems have been reported; for example: (a) Iyoda, M.; Ogura, E.; Hara, K.; Kuwatani, Y.; Nishikawa, H.; Sato, T.; Kikuchi, K.; Ikemoto, I.; Mori, T. *J. Mater. Chem*. **1999**, *9*, 335−337. (b) John, D. E.; Moore, A. J.; Bryce, M. R.; Batsanov, A. S.; Leech M. A.; Howard, J. A. K. *J. Mater. Chem*. **2000**, *10*, 1273−1279. (c) Hotta, S.; Kobayashi, H. *Synth. Met*. **1994**, *66*, 117−122. (d) Graf, D. D.; Duan, R. G.; Campbell, J. P.; Miller, L. L.; Mann, K. R. *J. Am. Chem. Soc*. **1997**, *119*, 5888−5899. (e) Kozaki, M.; Yonezawa, Y.; Okada, K. *Org. Lett*. **2002**, *4*, 4535−4538. (f) Frère, P.; Allain, M.; Elandaloussi, E. H.; Levillain, E.; Sauvage, F.-X.; Riou, A.; Roncali, J. *Chem. Eur. J*. **2002**, *8*, 784−792. (g) Yamashita, Y.; Tomura, M.; Zaman, M. B.; Imaeda, K. *Chem. Commun*. **1998**, 1657−1658. (h) Sedó, J.; Ventosa, N.; Ruiz-Molina, D.; Mas, M.; Molins, E.; Rovira, C.; Veciana, J. *Angew. Chem., Int. Ed*. **1998**, *37*, 330−333.

(7) X-ray structure analysis for oligo(amino-substituted electron donors): (a) Nelsen, S. F.; Ramm, M. T.; Ismagilov, R. F.; Nagy, M. A.; Trieber, D. A., II; Powell, D. R.; Chen, X.; Gengler, J. J.; Qu, Q.; Brandt, J. L.; Pladziewicz, J. R. *J. Am. Chem. Soc*. **1997**, *119*, 5900−5907. (b) Nelsen, S. F.; Ismagilov, R. F.; Gentile, K. E.; Powell, D. R. *J. Am. Chem. Soc*. **1999**, *121*, 7108−7114.

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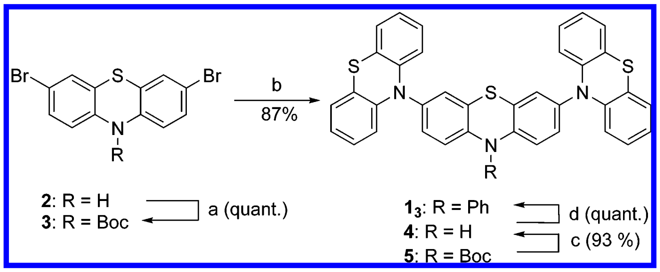
Phenothiazine trimer $\mathbf{1_3}$[8] was selectively synthesized through a cross-coupling reaction[9] of Boc-protected **3** with phenothiazine (Scheme 1).

Scheme 1. Synthesis of $\mathbf{1_3}$[a]



[a] Reagents and conditions: (a) $(Boc)_2O$, DMAP/CH_3CN, reflux. (b) Phenothiazine (2 equiv), $Pd(dba)_2$−$P(^tBu)_3$−NaO^tBu/toluene, reflux. (c) CH_3CO_2H, reflux. (d) Bromobenzene (1.1 equiv), $Pd(dba)_2$−$P(^tBu)_3$−NaO^tBu/toluene, reflux.

The cyclic voltammogram of $\mathbf{1_3}$ showed three reversible oxidation waves, $E_{1/2}(1) = +0.21$, $E_{1/2}(2) = +0.50$, and $E_{1/2}(3) = +0.78$ V vs Ag/AgCl in benzonitrile. The $E_{1/2}(1)$ value of $\mathbf{1_3}$ was lower than that of a reference of 10-phenylphenothiazine **6** (+0.38 V) by ~0.17 V, suggesting a stabilizing interaction in the radical cation.

Figure 1 shows the molecular structure of neutral $\mathbf{1_3}$ determined by X-ray structure analysis.[10] The three phenothiazine rings had butterfly structures.[11] The averaged bond angles around the nitrogen atoms deviated slightly from 120°; $\Delta\alpha_{av} = 1.3$, 2.3, and 1.7° for the central, left, and right nitrogen atoms, respectively, indicating p-character for the nitrogen lone pair orbitals.[12] These values are close to that of **6** ($\Delta\alpha_{av} = 0.8°$).[11b] Large dihedral angles were observed between planes A(B) and E(F), where plane E(F) is defined by three nitrogen-attached carbon atoms: C8, C9a″, and C10a″ (C2, C9a′, and C10a′). The angles were ~87° for A/E and ~86° for B/F, sufficiently large to prohibit conjugation between the phenothiazine rings. In fact, the UV−vis spectrum of $\mathbf{1_3}$ was very similar to that of **6** but with ca. triple the intensity ($\lambda_{max} = 256$ nm, $\epsilon \times 10^{-4}$ M^{-1} cm^{-1}: 4.45 for **6**, 15.2 for $\mathbf{1_3}$), indicating that $\mathbf{1_3}$ behaves like three noninteracting molecular assemblies in the neutral state.

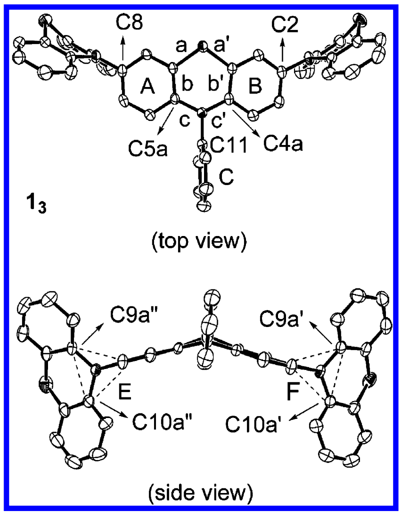


Figure 1. Molecular structure of neutral $\mathbf{1_3}$ at 50% ellipsoid level measured at 173 K. Selected bond lengths (Å) and dihedral angles (°): a,a′, 1.765(3), 1.763(3); b,b′, 1.401(4), 1.420(4); c,c′, 1.411(4), 1.420(4); A/B = 31.00, A/E(C8−C9a″−C10a″) = 87.33, B/F(C2−C9a′−C10a′) = 86.14, C/D(C4a−C5a−C11) = 86.09.

In contrast to the neutral state, the oxidized state showed unique characteristics. We isolated $\mathbf{1_3}^+$ using the method of Giffard and co-workers[13] through counterion exchange using $TBA^+PF_6^-$. The formula for the salt obtained from crystallization from acetonitrile was determined to be $\mathbf{1_3}^+\cdot PF_6^-\cdot 0.5CH_3CN$ from the elemental analysis.

Figure 2 shows the UV−vis absorption spectrum of $\mathbf{1_3}^+$. A strong absorption band newly appeared at $\lambda_{max} = 945$ nm ($\epsilon = 2.83 \times 10^4$). The spectrum is totally different from that of $\mathbf{6}^+$ ($\epsilon_{517} = 9.54 \times 10^3$),[14] suggesting a new electronic state of $\mathbf{1_3}^+$ on the basis of the trimeric structure.

Figure 3 shows the molecular structure determined by X-ray analysis.[10] The acetonitrile solvent could not be observed because of large disorders in the PF_6^- counterion parts (not shown). The conformation of $\mathbf{1_3}^+$ was distinctly different from that of $\mathbf{1_3}$. The central phenothiazine of $\mathbf{1_3}^+$ was almost flat, whereas the outer two rings had butterfly structures as observed in the neutral $\mathbf{1_3}$, indicating that the radical cation is localized mainly on the central ring.[15] The

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(8) Compound data for $\mathbf{1_3}$ and $\mathbf{1_3}^+$. $\mathbf{1_3}$: yellow needles; mp 277.0−279.0 °C; ^{1}H NMR (400 MHz, C_6D_6) δ 6.19 (d, 2H, $J = 8.8$ Hz), 6.27 (d, 4H, $J = 7.3$ Hz), 6.51 (dd, 2H, $J = 8.8$, 2.4 Hz), 6.56−6.64 (m, 9H), 6.73 (d, 2H, $J = 2.2$ Hz), 6.92 (dd, 4H, $J = 7.1$ Hz, 1.7 Hz), 7.01−7.11 (m, 4H); IR (KBr, cm^{-1}) 1595, 1570, 1460, 1441, 1298, 1259, 1234, 1128, 1119, 1043, 924, 745, 698, 669, 546; HRMS (FAB) m/z calcd for $C_{42}H_{27}N_3S_3$ 669.1367, found 669.1382. $\mathbf{1_3}^+\cdot PF_6^-\cdot 0.5CH_3CN$: black plates, mp (decomp.) ca. 257 °C; EPR $g = 2.0041$ ($\nu_0 = 9.2455$ three broad lines with $a_N = 0.55$ mT in butyronitrile at room temperature); IR (KBr, cm^{-1}) 1595, 1568, 1474, 1460, 1445, 1281, 1263, 1246, 1165, 1128, 1076, 1032, 843, 766, 737, 698, 669, 637, 557; MS (FAB) 669 ($C_{42}H_{27}N_3S_3^+$); Anal. Calcd for $\mathbf{1_3}^+\cdot PF_6^-\cdot 0.5CH_3CN$: C 61.82, H 3.44, N 5.87. Found C 62.01, H 3.33, N 5.90.

(9) Hartwig, J. F.; Kawatsura, M.; Hauck, S. I.; Shaughnessy, K. H.; Alcazar-Roman, L. M. *J. Org. Chem.* **1999**, *64*, 5575−5580.

(10) Crystallographic data for $\mathbf{1_3}\cdot CH_2Cl_2$: colorless plate, triclinic, space group P-1 (#2), $a = 10.713(1)$ Å, $b = 12.332(2)$ Å, $c = 15.377(3)$ Å, $\alpha = 82.11(1)°$, $\beta = 82.15(1)°$, $\gamma = 62.851(8)°$, $V = 1784.2(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.383$ g/cm^3, $2\theta_{max} = 55.0°$, Mo Kα radiation (0.71070 Å), $T = 173$ K, 17 451 measured reflections, 7649 unique reflections, 7428 observed reflections ($I > -10\sigma$, all data), 489 parameters, $R_1(I > 2\sigma) = 0.078$, $R_w(I > -10\sigma) = 0.173$, GOF = 0.926. Crystallographic data for $\mathbf{1_3}^+\cdot PF_6^-\cdot 0.5CH_3CN$: black plate, monoclinic, space group $C2$ (#5), $a = 27.60(2)$ Å, $b = 9.129(8)$ Å, $c = 15.39(1)$ Å, $\beta = 94.65(1)°$, $V = 3864.7(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.400$ g/cm^3, $2\theta_{max} = 55.0°$, Mo Kα radiation (0.71070 Å), $T = 113$ K, 15 203 measured reflections, 4636 unique reflections, 4515 observed reflections ($I > -10\sigma$, all data), 562 parameters, $R_1(I > 2\sigma) = 0.087$, $R_w(I > -10\sigma) = 0.234$, GOF = 0.934. CCDC 239333 ($\mathbf{1_3}$) and CCDC 239334 ($\mathbf{1_3}^+$).

(11) (a) McDowell, J. J. H. *Acta Crystallogr.* **1976**, *B32*, 5−10. (b) Moerman, B.; Ouwerkerk, M.; Kroon, J. *Acta Crystallogr.* **1985**, *C41*, 1205−1208.

(12) Nelsen, S. F. *J. Org. Chem.* **1984**, *49*, 1891−1897.

(13) Giffard, M.; Mabon, G.; Leclair, E.; Mercier, N.; Allain, M.; Gorgues, A.; Molinié, P.; Neilands, O.; Krief, P.; Khodorkovsky, V. *J. Am. Chem. Soc.* **2001**, *123*, 3852−3853.

(14) Wagner, E.; Filipek, S.; Kalinowski, M. K. *Monatsh. Chem.* **1988**, *119*, 929−932.

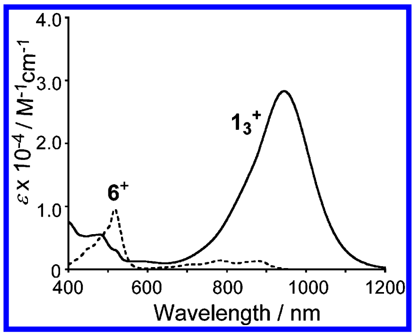

Figure 2. UV−vis spectrum of $\mathbf{1_3}^+$: solid line for $\mathbf{1_3}^+\cdot PF_6^-\cdot 0.5CH_3CN$ and dashed line for $\mathbf{6}^+\cdot PF_6^-$ in methylene chloride.

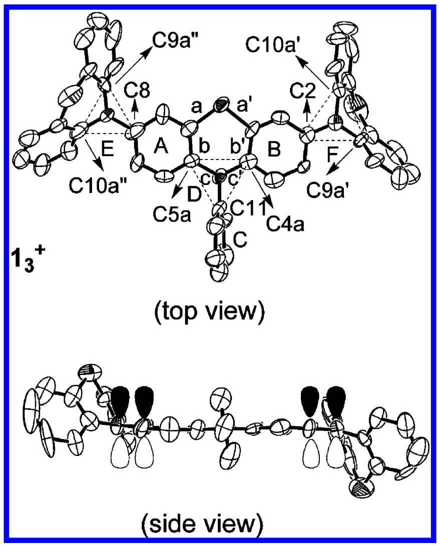

Figure 3. Molecular structure of $\mathbf{1_3}^+$ at 50% ellipsoid level determined at 113 K. Selected bond lengths (Å) and dihedral angles (°); a,a′, 1.744(9), 1.727(10), b,b′, 1.411(13), 1.424(12), c,c′, 1.395(11), 1.398(11); A/B = 2.76, A/E(C8−C9a″−C10a″) = 10.85, B/F(C2−C9a′−C10a′) = 5.39, C/D(C4a−C5a−C11) = 82.44.

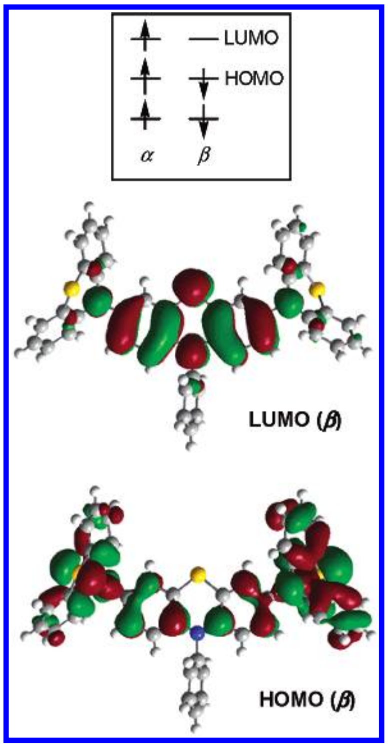

Figure 4. Molecular orbitals of HOMO (β) and LUMO (β) for $\mathbf{1_3}^+$ (TD-UB3LYP/6-31G*).

averaged bond angle around the central nitrogen atom was 120° ($\Delta\alpha_{av} = 0.0°$), whereas those of the outer nitrogen atoms were a little higher, $\Delta\alpha_{av} = 1.3°$ for the left and 0.2° for the right nitrogen atoms. More importantly, the dihedral angles between planes A(B) and E(F) were remarkably small for $\mathbf{1_3}^+$, 11° for A/E and 5° for B/F (Figure 3), enabling orbital interaction between the p-orbitals of the C2(C8) atoms and the lone pair orbitals of the nitrogen atoms (Figure 3, side view). The advantage of this rather surprising structure is conjugated stabilization of $\mathbf{1_3}^+$ without severe steric repulsion between the phenothiazine rings. The conceivable radical cation localized on the outer ring(s) obviously cannot achieve this stabilization because of the large dihedral angle between the outer phenothiazine radical cation and the benzo-ring of the central phenothiazine, as recognized from the large dihedral angle between planes C and D (C4a−C5a−C11 plane). Electron removal from the central phenothiazine ring must be facilitated by the simultaneous or rapid bond rotation around the C2,8-N(outer phenothiazines), giving stabilized $\mathbf{1_3}^+$, compatible with the lower and reversible oxidation potential of $\mathbf{1_3}$.

The structural feature described above suggests that the observed new absorption at 945 nm is an intramolecular CT band from the outer phenothiazines to the inner radical cation through the nitrogen lone pair orbitals. To clarify this, we performed theoretical calculations [TD-UB3LYP/6-31G*] using the Gaussian 03 program package.[16] The geometry was taken from the X-ray analysis. The calculated absorption maximum was 954 nm with an oscillator strength $f = 0.204$ for the first excited state; the absorption had a main

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(15) (a) Singhabhandhu, A.; Robinson, P. D.; Fang, J. H.; Geiger, W. E., Jr. *Inorg. Chem.* **1975**, *14*, 318−323. (b) Von Dreele, R. B.; Harris, J. *Acta Crystallogr.* **1983**, *C39*, 170−173.

(16) In the TD calculation, 50 highest occupied and 50 lowest vacant orbitals were considered. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.01; Gaussian, Inc.: Pittsburgh, PA, 2003.

contribution of HOMO (β) → LUMO (β) transition with a coefficient of 0.91 (Figure 4), compatible with the assignment of the CT-band from the outer to inner phenothiazine rings.

In summary, we have demonstrated that the neutral trimeric phenothiazine $\mathbf{1_3}$ can be approximated as three noninteracting phenothiazines, whereas the oxidized $\mathbf{1_3}^+$ receives a surprisingly large geometrical change and behaves as a conjugated trimeric phenothiazine. Further study, including higher oligomers and dendrimers and the role of $\mathbf{1_3}^+$ structure in those assemblies, is in progress.

Supporting Information Available: Synthetic procedure for $\mathbf{1_3}$ and $\mathbf{1_3}^+$ and X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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