Tiara Structures

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Dodecanuclear-Ellipse and Decanuclear-Wheel Nickel(II) Thiolato Clusters with Efficient Femtosecond Nonlinear Absorption[**]

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Thiolate ligands have been of longstanding interest for a variety of reasons: 1) their diverse binding modes give rise to an array of bonding motifs that are of fundamental importance in coordination chemistry,[1] 2) metal–thiolate interactions are key elements of numerous metalloproteins and play a crucial role in the broader field of bioinorganic chemistry,[2] and 3) thiolate-mediated magnetic coupling is an essential component in novel molecular magnets.[3] Amongst the range of metal thiolate-derived structures, the synthesis, structure, and magnetic properties of toroidal (or tiara-like) architectures have raised considerable interest.[4,5] However, most of the known tiara-like $[M(\mu\text{-SR})]_n$ (M = Ni, Pd) clusters to date have been constructed by single thiolate ligands and possess geometrically similar ring systems,[4] which has restricted, to some extent, the abundance of examples and structural diversity of the tiara family.

The development of high-performance molecular materials with optimized nonlinear optical (NLO) properties has also been the focus of much current research.[6,7] Previous studies have demonstrated that the presence of large π-electron delocalization and a symmetrical planar structure play crucial roles in determining the properties of nonlinear chromophores.[6a–c,e,7h,k,8] Curiously, though, despite the quasi-aromatic nature of the bonding that has been proposed in nickel toroidal species,[4d] their optical properties are little explored; in particular, no study of the NLO properties is extant.

We present here the synthesis of the largest tiara-like nickel(II)–thiolate cluster thus far by a novel route that employs two different thiolate bridges, structural studies that reveal an unprecedented elliptical structure for $[\mathrm{Ni}(\mu\text{-S}t\mathrm{Bu})(\mu\text{-etet})]_{12}$ (etet = 2-ethylthioethanethiolate) and two new decanuclear-wheel nickel(II)–thiolato clusters $[\mathrm{Ni}(\mu\text{-S}t\mathrm{Bu})(\mu\text{-pyet})]_{10}$ (pyet = 2-(2-mercaptoethyl)pyridine) and $[\mathrm{Ni}(\mu\text{-S}t\mathrm{Bu})(\mu\text{-atet})]_{10}$ (atet = 2-aminoethanethiol), and the first NLO studies of examples from this important class of molecules, together with time-dependent DFT studies that shed light on the optical behavior.

The reaction of $\mathrm{NiCl_2{\cdot}6H_2O}$ with 1 equivalent K(etet) gave, after work-up, separable $[(\mathrm{CH_3C_6H_5})\subset\{\mathrm{Ni}(\mu\text{-S}t\mathrm{Bu})(\mu\text{-etet})\}_{10}]$ (**1a**) and $[\mathrm{Ni}(\mu\text{-S}t\mathrm{Bu})(\mu\text{-etet})]_{12}{\cdot}(\mathrm{CH_3C_6H_5})_2$ (**1b**), whereas similar reactions with K(pyet) or K(atet), instead of K(etet), afforded $[(\mathrm{CH_3C_6H_5})\subset\{\mathrm{Ni}(\mu\text{-S}t\mathrm{Bu})(\mu\text{-pyet})\}_{10}]{\cdot}(\mathrm{CH_3C_6H_5})_4$ (**2**) and $[(0.5\,\mathrm{CH_3C_6H_5})\subset\{\mathrm{Ni}(\mu\text{-S}t\mathrm{Bu})(\mu\text{-atet})\}_{10}]{\cdot}(\mathrm{CH_3C_6H_5})_2$ (**3**), respectively. The atomic arrangements and stoichiometries of **1a**, **1b**, **2**, and **3** were unequivocally established from low-temperature CCD area-detector X-ray diffraction studies. The single-crystal X-ray analysis of **1b** reveals a heretofore unknown dodecagonal-ellipse $\mathrm{Ni_{12}S_{24}}$ framework, as displayed in Figure 1. The top view (Figure 1 a) of the cyclic $\mathrm{Ni_{12}S_{24}}$ architecture shows that edge-fusion of the 12 localized planar $[\mathrm{NiS_4}]$ subunits along opposite nonbonding S–S edges gives rise to a triple-layer elliptical geometry that approximately conforms to pseudo-D_2 symmetry. The transannular Ni⋯Ni distances of **1b** are in the range of 11.343(6)–13.528(7) Å, while the dihedral angles between adjoining $[\mathrm{NiS_2}]$ planes vary from 140.32 to 157.84° because of the unsymmetrical elliptical geometry of this unique 12-membered Ni ring. The side view (Figure 1 b) of the toroid **1b**

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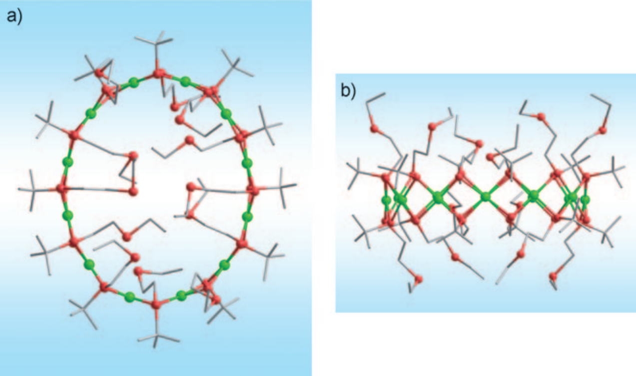

Figure 1. Molecular view of $[Ni(\mu\text{-S}t\text{Bu})(\mu\text{-etet})]_{12}\cdot(CH_3C_6H_5)_2$ (**1b**): Ni green, S red, C gray. Neighboring interatomic distances [Å]: Ni–S 2.192(3)–2.248(4) (av: 2.217), Ni–Ni 3.140(1)–3.257(1) (av: 3.212). The hydrogen atoms and two toluene solvent molecules outside the $Ni_{12}S_{24}$ toroid are omitted for clarity.

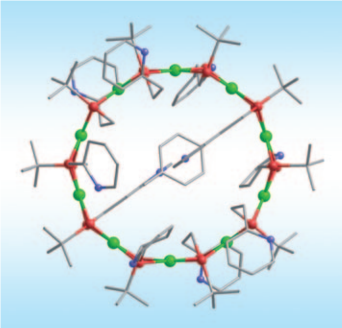

Figure 2. Molecular view of $[(CH_3C_6H_5)\subset\{Ni(\mu\text{-S}t\text{Bu})(\mu\text{-pyet})\}_{10}]\cdot(CH_3C_6H_5)_4$ (**2**): Ni green, S red, N blue, C gray. Neighboring interatomic distances [Å]: Ni–S 2.1870(8)–2.2188(9) (av: 2.2067), Ni–Ni 3.1488(2)–3.1771(2) (av: 3.1606). The hydrogen atoms and four toluene solvent molecules outside the $Ni_{10}S_{20}$ toroid are omitted for clarity.

shows a virtually planar nonbonding Ni_{12} ring sandwiched between two approximately coplanar nonbonding S_{12} rings. The two kinds of thiolate ligands, etet and S*t*Bu, are situated alternately above and below the Ni_{12} plane, with all *t*Bu groups oriented away from the ring. The etet substituents display three distinct orientations; six of the etet ligands project upward or downward, and four etets incline at approximately 45° to the Ni_{12} ring, while the remaining two etet groups penetrate the cavity of the $Ni_{12}S_{24}$ toroid and sustain the tiara architecture in the absence of co-crystallized solvent molecules within the Ni_{12} ring. The toroidal $Ni_{10}S_{20}$ core geometries of **2** and **3** are shown in Figures 2 and S5 (see the Supporting Information), with pyet (or atet) and S*t*Bu ligands bridging adjacent Ni atoms alternately above and below the Ni_{10} ring. In contrast to the $Ni_{12}S_{24}$ ellipsoid of **1b**, one toluene molecule is encapsulated in the Ni_{10} cavity of **2** and **3**, and is situated approximately in the Ni_{10} plane, tilted from coplanarity by 29.434(2)° for **2** (18.338(1)° for **3**), which results in the toroidal $Ni_{10}S_{20}$ core approximating a circular shape (transannular Ni···Ni distances are nearly constant (9.974(9)–10.397(9) Å in **2**, and 10.04(1)–10.46(1) Å in **3**)). As was the case for $[Ni(\mu\text{-S}t\text{Bu})(\mu\text{-etet})]_{12}\cdot(CH_3C_6H_5)_2$ (**1b**), the *t*Bu groups are all oriented away from the $Ni_{10}S_{20}$ toroid, and the pyet/atet substituents project above and below the plane of the toroid, except for two pyet/atet ligands whose amidocyanogen arms apparently clamp the encapsulated toluene molecule from above and below. Dihedral angles between adjacent $[NiS_2]$ planes are similar (141.7–146.88° for **2**, and 138.1–151.0° for **3**), and close to the interior angle of an idealized decagon, consistent with the pseudo-D_{5d} symmetry for the $Ni_{10}S_{20}$ tiara-geometry of **2** and **3**.

Z-scan measurements on the toroid clusters **1b**, **2**, and **3** were performed in the wavelength range 530–1300 nm (see Figures 3 and S6). The dominant NLO process is presumed to be one-photon absorption in the tail of the absorption curve, followed by excited-state absorption. Under such circumstances, the two-photon absorption cross-sections measured in the *Z*-scan experiments should be considered effective values only. Assuming that the pulse duration (≈150 fs) is much shorter than the lifetime of the excited state, the effective two-photon cross-section can be approximated as $\sigma_{2,\text{eff}} = 0.5\,\sigma\,\sigma_{\text{ex}}\,t_p$, where σ is the one-photon cross-section, σ_{ex} is the excited state cross-section and t_p is the pulse duration. Figures 3 and S6 illustrate the results of calculations of the excited-state cross-section spectra. All three compounds show similar spectra that peak at approximately 700 nm with a

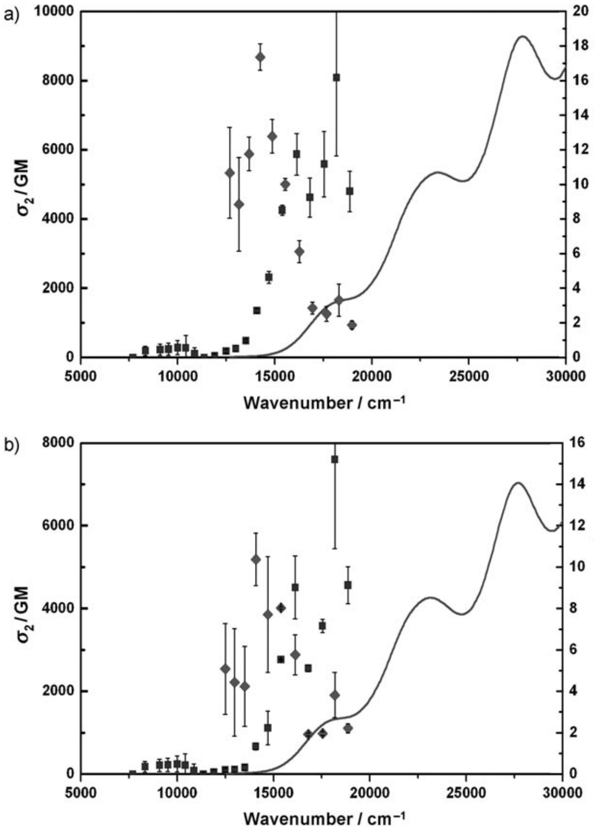

Figure 3. Experimental two-photon absorption profiles for a) cluster **2** (1.48×10^{-4} mol L^{-1} in DMF) and b) cluster **3** (1.56×10^{-4} mol L^{-1} in DMF). ■ σ_2, ◆ σ_{ex}, —— σ.

cross-section of approximately 10^{-17} cm^2. This is of the same order of magnitude as those obtained for many other cluster compounds in nanosecond experiments,[7g–j] but further substantial comment is not warranted because ns experiments are usually dominated by long-lived triplet excitations, whereas fs measurements are dominated by much shorter-lived singlet excited species. Nevertheless, a preliminary internal comparison of the NLO performance of **1b**, **2**, and **3** with tiara-like geometries can be undertaken. Their coplanar Ni_nS_{2n} ($n = 10$, 12) geometries and Ni–S π bonding orbitals distributed throughout the Ni_nS_{2n} ($n = 10$, 12) tiara-like structures should influence the fs NLO merit of these toroidal thiolate clusters. Although the Ni^{II} thiolate clusters **1b**, **2**, and **3** are constructed from the same [NiS_4] subunits and possess similar toroidal frameworks, the observed NLO behavior of **1b**, **2**, and **3** are distinct. Specifically, the nonlinear absorption maxima of **2** and **3** are greater than that of **1b** at around 630 nm, suggesting superiority of the $Ni_{10}S_{20}$-centered coplanar geometry.

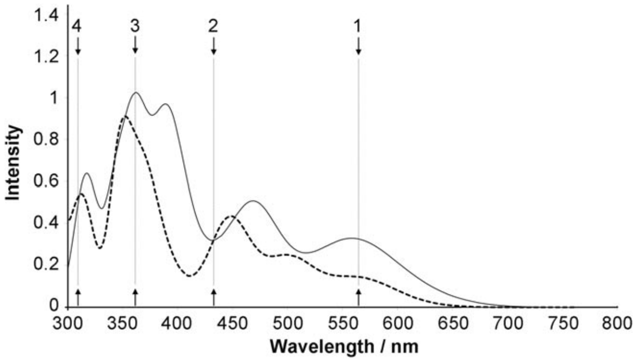

Figure 4. "Synthetic" spectra obtained from TD-DFT calculations, at the SAOP/TZP level of theory, of transition energies and relative oscillator strengths for the PBE/TZP optimized {Ni(μ-SMe)$_2$}$_n$ models (n = 10: -----, 12: ——). Peak shapes were obtained by Gaussian broadening of up to 700 summed dipole-allowed transitions across the wavelength range of interest. Arrows and vertical lines superimposed upon the graph show the observed wavelengths of the experimental spectral peaks.

DFT calculations, using the Amsterdam Density Functional program suite ADF2008.01,[9] were performed on simplified models of compounds **1b**, **2**, and **3**, to shed light on the structural diversity and optical behavior of these novel species. Geometry optimization at the PBE/TZP level of theory was undertaken on C_2-, D_{5d}- and D_2-symmetric structures analogous to **1b**, **2**, and **3**, respectively, but with all bridging groups replaced by μ-SMe groups for the purposes of computational expediency. The corresponding key data for bond lengths and angles of the optimized geometries (see Table S2 in the Supporting Information) of **1b** in D_2- and **2** and **3** in D_{5d}-symmetrical models are consistent with those of their X-ray diffraction data. Spectroscopy of the PBE/TZP optimized "permethylated" models described above was computed by time-dependent DFT (TD-DFT), using the SAOP/TZP level of theory. A summary of the results is presented in Figures 4, 5, S9, S10, and Table S3. We find that the observed lower-energy features in the experimental spectra (λ > 400 nm) are attributable to excitation from occupied Ni d-character orbitals to vacant NiS σ*-type orbitals, while the spectral features at wavelengths shorter than 400 nm arise predominantly from more deeply submerged occupied orbitals (principally S p in character) to the same vacant NiS σ* orbitals. These calculations necessarily relate to the clusters in vacuum, because solvent correction using triple-zeta-plus-polarization basis sets (as above) was judged to be prohibitive in regard to the TD-DFT computation required for the theoretical spectra. Solvent-corrected (polarized continuum model, or PCM) TD-DFT

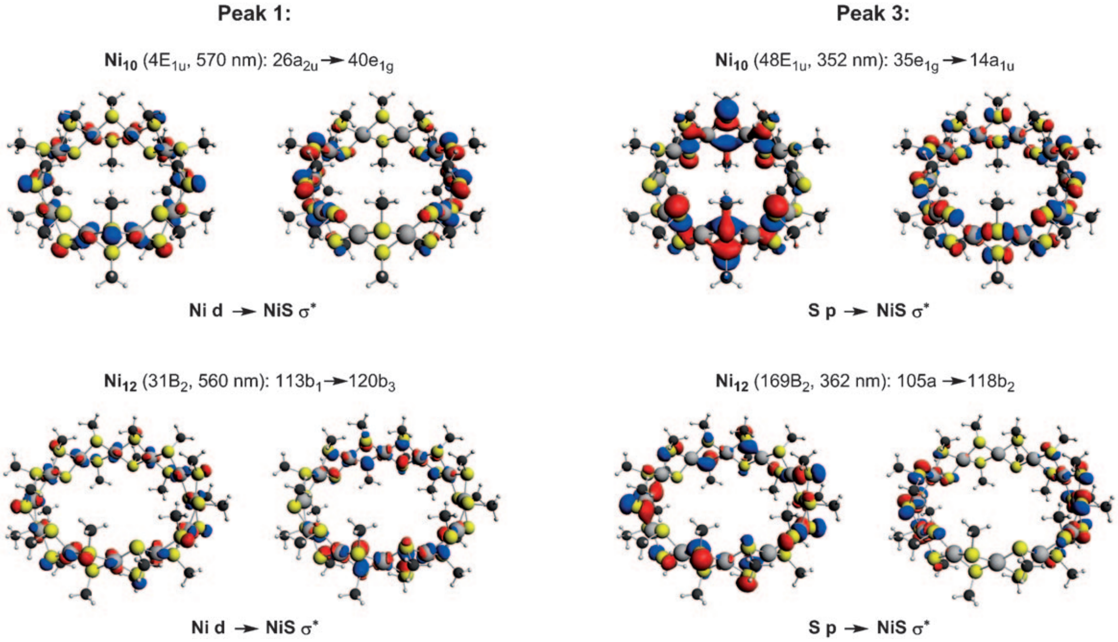

Figure 5. Assignment of the absorption peaks 1 and 3 of the D_{5d}-symmetric {Ni(μ-SMe)$_2$}$_{10}$ model and the D_2-symmetric {Ni(μ-SMe)$_2$}$_{12}$ model in vacuum. The orbitals are obtained at the PBE/TZP level.

calculations on the full compound **3** were, however, pursued independently by using the Gaussian program suite[10] at the B3-LYP/LANL2DZ level of theory with a dielectric constant of $\varepsilon = 2.24$ appropriate to toluene. The latter calculations gave a good fit with the observed spectral features in terms of computed peak positions.

In summary, this study demonstrates that a geometrically unprecedented dodecanuclear-ellipse $[Ni(\mu\text{-S}t\text{Bu})(\mu\text{-etet})]_{12}\cdot(CH_3C_6H_5)_2$ and two decanuclear-wheel nickel(II)–thiolato clusters can be constructed by stepwise introduction of two kinds of different thiolates to a nickel(II) center, which adds a new dimension to nickel toroid chemistry. The first experimental assessment of fs wavelength-dependent nonlinear optical behavior and a theoretical study of the linear optical performance for this new class of NLO chromophore have been conducted, the results suggesting that Ni−S π bonds play a crucial role in both the stabilization of such dodeca- and decanuclear tiara-like geometries, their linear optical properties, and, by implication, their strong fs nonlinear optical behavior. An in-depth study probing the mechanism of both the fs and ns optical nonlinearity of these Ni_nS_{2n} toroids is currently underway.

Experimental Section

Details of the chemical synthesis, spectroscopic characterization, structural, theoretical, and nonlinear optical studies are given in the Supporting Information.

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[1] For selected reviews, see: a) P. J. Blower, J. R. Dilworth, *Coord. Chem. Rev.* **1987**, *76*, 121–185; b) D. W. Stephan, T. T. Nadasdi, *Coord. Chem. Rev.* **1996**, *147*, 147–208; c) L. C. Song, *Acc. Chem. Res.* **2005**, *38*, 21–28; d) H. Fleischer, *Coord. Chem. Rev.* **2005**, *249*, 799–827; e) R. Y. C. Shin, L. Y. Goh, *Acc. Chem. Res.* **2006**, *39*, 301–313; f) X. Y. Tang, H. X. Li, J. X. Chen, Z. G. Ren, J. P. Lang, *Coord. Chem. Rev.* **2008**, *252*, 2026–2049.

[2] a) E. I. Stiefel, K. Matsumoto, *Transition Metal Sulfur Chemistry: Biological and Industrial Significance*, ACS, Washington, **1996**; b) I. G. Dance, K. Fisher, *Prog. Inorg. Chem.* **1994**, *41*, 637–803; c) S. C. Lee, R. H. Holm, *Chem. Rev.* **2004**, *104*, 1135–1157; d) G. Henkel, B. Krebs, *Chem. Rev.* **2004**, *104*, 801–824; e) J. A. Kovacs, L. M. Brines, *Acc. Chem. Res.* **2007**, *40*, 501–509; f) Y. Ohki, Y. Ikagawa, K. Tatsumi, *J. Am. Chem. Soc.* **2007**, *129*, 10457–10465; g) T. Matsumoto, Y. Nakaya, N. Itakura, K. Tatsumi, *J. Am. Chem. Soc.* **2008**, *130*, 2458–2459; h) Y. Ohki, K. Yasumura, K. Kuge, S. Tanino, M. Ando, Z. L. Li, K. Tatsumi, *Proc. Natl. Acad. Sci. USA* **2008**, *105*, 7652–7657.

[3] a) M. Z. Zhu, C. M. Aikens, M. P. Hendrich, R. Gupta, H. F. Qian, G. C. Schatz, R. C. Jin, *J. Am. Chem. Soc.* **2009**, *131*, 2490–2492; b) R. Llusar, S. Triguero, V. Polo, C. Vicent, C. J. Gomez-Garcia, O. Jeannin, M. Fourmigue, *Inorg. Chem.* **2008**, *47*, 9400–9409; c) L. M. Brines, J. Shearer, J. K. Fender, D. Schweitzer, S. C. Shoner, D. Barnhart, W. Kaminsky, S. Lovell, J. A. Kovacs, *Inorg. Chem.* **2007**, *46*, 9267–9277.

[4] a) C. Zhang, S. Takada, M. Kölzer, T. Matsumoto, K. Tatsumi, *Angew. Chem.* **2006**, *118*, 3852–3856; *Angew. Chem. Int. Ed.* **2006**, *45*, 3768–3772, and references therein; b) S. A. Ivanov, M. A. Kozee, W. A. Merrill, S. Agarwal, L. F. Dahl, *J. Chem. Soc. Dalton Trans.* **2002**, 4105–4115, and references therein; c) Z. Q. Yang, A. B. Smetana, C. M. Sorensen, K. J. Klabunde, *Inorg. Chem.* **2007**, *46*, 2427–2431, and references therein; d) A. Datta, N. S. John, G. U. Kulkarni, S. K. Pati, *J. Phys. Chem. A* **2005**, *109*, 11647–11649.

[5] a) C. L. Ma, Q. F. Zhang, R. F. Zhang, D. Q. Wang, *Chem. Eur. J.* **2006**, *12*, 420–428; b) F. E. Hahn, C. Ochs, T. Lügger, R. Fröhlich, *Inorg. Chem.* **2004**, *43*, 6101–6107; c) O. L. Sydora, P. T. Wolczanski, E. B. Lobkovsky, E. Rumberger, D. N. Hendrickson, *Chem. Commun.* **2004**, 650–651; d) O. L. Sydora, P. T. Wolczanski, E. B. Lobkovsky, *Angew. Chem.* **2003**, *115*, 2789–2791; *Angew. Chem. Int. Ed.* **2003**, *42*, 2685–2687; e) D. Sellmann, F. Geipel, F. W. Heinemann, *Chem. Eur. J.* **2002**, *8*, 958–966.

[6] For selected reviews on third-order NLO materials, see: a) C. Zhang, Y. L. Song, X. Wang, *Coord. Chem. Rev.* **2007**, *251*, 111–141; b) M. O. Senge, M. Fazekas, E. G. A. Notaras, W. J. Blau, M. Zawadzka, O. B. Locos, E. M. Ni Mhuircheartaigh, *Adv. Mater.* **2007**, *19*, 2737–2774; c) Y. Chen, M. Hanack, Y. Araki, O. Ito, *Chem. Soc. Rev.* **2005**, *34*, 517–529; d) C. E. Powell, M. G. Humphrey, *Coord. Chem. Rev.* **2004**, *248*, 725–756; e) G. de La Torre, P. Vazquez, F. Agullo-Lopez, T. Torres, *Chem. Rev.* **2004**, *104*, 3723–3750; f) J. L. Brédas, C. Adant, P. Tackx, A. Persoons, B. M. Pierce, *Chem. Rev.* **1994**, *94*, 243–278.

[7] For selected reports of third-order NLO studies, see: a) J. M. Hales, S. J. Zheng, S. Barlow, S. R. Marder, J. W. Perry, *J. Am. Chem. Soc.* **2006**, *128*, 11362–11363; b) Y. Matsuo, M. Maruyama, S. S. Gayathri, T. Uchida, D. M. Guldi, H. Kishida, A. Nakamura, E. Nakamura, *J. Am. Chem. Soc.* **2009**, *131*, 12643–12649; c) H. W. Hou, Y. L. Wei, Y. L. Song, L. W. Mi, M. S. Tang, L. K. Li, Y. T. Fan, *Angew. Chem.* **2005**, *117*, 6221–6228; *Angew. Chem. Int. Ed.* **2005**, *44*, 6067–6074; d) H. Ma, A. K. Y. Jen, *Adv. Mater.* **2001**, *13*, 1201–1205; e) B. Babgi, L. Rigamonti, M. P. Cifuentes, T. C. Corkery, M. D. Randles, T. Schwich, S. Petrie, R. Stranger, A. Teshome, I. Asselberghs, K. Clays, M. Samoc, M. G. Humphrey, *J. Am. Chem. Soc.* **2009**, *131*, 10293–10307; f) R. L. Roberts, T. Schwich, T. C. Corkery, M. P. Cifuentes, K. A. Green, J. D. Farmer, P. L. Low, T. B. Marder, M. Samoc, M. G. Humphrey, *Adv. Mater.* **2009**, *21*, 2318–2322; g) C. Zhang, Y. Cao, J. F. Zhang, S. C. Meng, T. Matsumoto, Y. L. Song, J. Ma, Z. X. Chen, K. Tatsumi, M. G. Humphrey, *Adv. Mater.* **2008**, *20*, 1870–1875; h) C. Zhang, Y. L. Song, F. E. Kühn, Y. X. Wang, X. Q. Xin, W. A. Herrmann, *Adv. Mater.* **2002**, *14*, 818–822; i) M. Feliz, J. M. Garriga, R. Llusar, S. Uriel, M. G. Humphrey, N. T. Lucas, M. Samoc, B. Luther-Davies, *Inorg. Chem.* **2001**, *40*, 6132–6138; j) A. Mateo-Alonso, K. Iliopoulos, S. Couris, M. Prato, *J. Am. Chem. Soc.* **2008**, *130*, 1534–1535; k) K. J. Thorley, J. M. Hales, H. L. Anderson, J. W. Perry, *Angew. Chem.* **2008**, *120*, 7203–7206; *Angew. Chem. Int. Ed.* **2008**, *47*, 7095–7098.

[8] a) J. W. Perry, K. Mansour, I. Y. S. Lee, X. L. Wu, P. V. Bedworth, C. T. Chen, D. Ng, S. R. Mardar, P. Miles, T. Wada, M. Tian, H. Sasabe, *Science* **1996**, *273*, 1533–1536; b) D. G. McLean, R. L. Sutherland, M. C. Brant, D. M. Brandelik, P. A. Fleitz, T. Pottenger, *Opt. Lett.* **1993**, *18*, 858–860.

[9] E. J. Baerends et al., ADF2008.01, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com.

[10] M. J. Frisch, et al., Gaussian 03, Revision D. 01, Gaussian, Inc.: Wallingford, CT, **2004**.