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Conversion of a [6]Helicene into an [8]Helicene and a Helical 1,10-Phenanthroline Ligand

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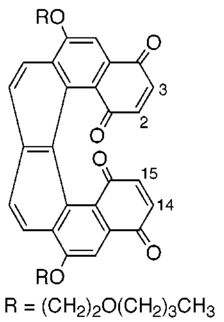
While until recently helicenes have been available in only small amounts[1] and with limited functionality,[4] ca. 25 g of [5]helicenebisquinones and 6- and 7-ring analogues such as **1** and **2** can be made easily in the laboratory and resolved into their enantiomers.[3,5−7] [8]-Helicenes, however, remain rare. In fact, only six appear to have been made: **3**,[8] **4**,[9] **5**,[10] and three derivatives of **3** that were the precursors of **4**.[2c,9,11]



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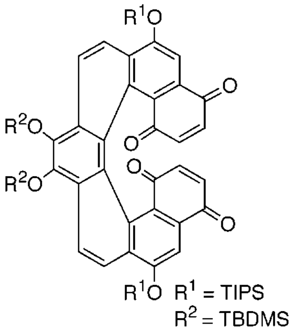

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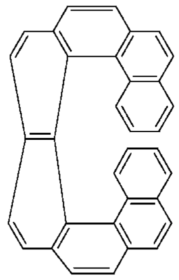

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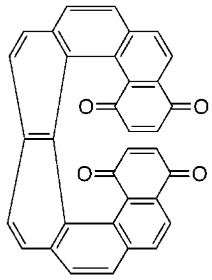

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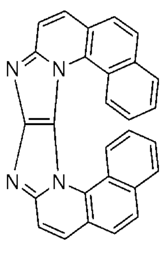

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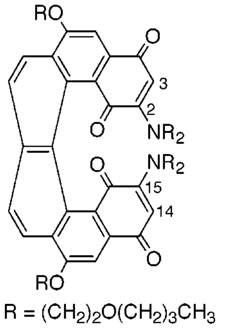
The question considered here is whether two previous discoveries could be combined to elaborate a [6]helicene into an [8]helicene. One discovery is that, in the presence of Cu(OAc)$_2$, secondary amines add to [6]helicenebisquinone **1** to produce adducts specifically of structure **6**.[3,12] The selectivity for reaction at carbons 2 and 15, rather than at 3 and 14, is so high that pyrrolidine gives a 92% yield of only this one adduct, and its purity is >95%.[3] Other nucleophiles exhibit similar selectivity,[13] the origin of which appears to be understood.[3] The other discovery is that 1,2-phenylenediamine combines with 1,4-naphthoquinone in acetic acid to give 5-hydroxybenzo[*a*]phenazine, **7**,[14] a transformation that fuses a quinoxaline to the naphthalene core. An analogous reaction with bisquinone **1** would fuse two such rings to the [6]helicene. Moreover, if it occurred with the same regioselectivity, simple reagents should convert a derivative of [6]helicene that is itself easy to obtain into a derivative of [8]helicene. Since bisquinone **1** can be obtained optically pure,[3] any [8]helicene made from it would be too. We report here the realization of this possibility. We also show how the resulting [8]helicene can be transformed into a bis-*o*-quinone, and this, in turn, into a bis-bidentate ligand.



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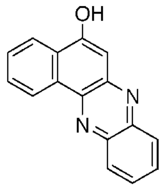

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Results and Discussion

Synthesis of [8]Helicenes. As summarized in Scheme 1, combining levorotatory bisquinone (*M*)-**1** with 1,2-phenylenediamine in the presence of Cu(OAc)$_2$ and air gives adduct **8** in 75% yield, and this, when heated in acetic acid, cyclizes to give [8]helicene derivative **9**.

In contrast to **7**, which is present in solution primarily as the phenol tautomer, **9** in solution is present mainly as the ketone (or vinylogous lactam). The evidence rests in part on the properties of the diacetate **10**, prepared by treating **9** with Ac$_2$O in Et$_3$N (see Scheme 1). Since the diacetate shows in its UV−vis absorption spectrum (displayed in the Supporting Information) a longest wavelength maximum at 460 nm,[15,16] in its ^{13}C NMR spectrum only one resonance at low field (δ 167.3 ppm), which must be assigned to the carbonyl of the acetate,

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[1] Stilbene photocyclizations,[2a] commonly used to prepare helicenes,[2b] must be carried out using solutions that are dilute,[2a,c] and they are inhibited by amino, nitro, and other functional groups that relax the singlet excited state of the stilbene.[2a] The majority of helicene syntheses that do not use light have produced examples that racemize at a significant rate at room temperature (see ref 3, footnotes 1−3 and 6).

(2) (a) Mallory, F. B.; Mallory, C. W. *Organic Reactions*; Wiley: New York, 1984; Vol. 30, p 1. (b) Laarhoven, W. H.; Prinsen, W. J. C. *Top. Curr. Chem.* **1984**, *125*, 63. (c) Liu, L.; Yang, B.; Katz, T. J.; Poindexter, M. K. *J. Org. Chem.* **1991**, *56*, 3769.

(3) Katz, T. J.; Liu, L.; Willmore, N. D.; Fox, J. M.; Rheingold, A. L.; Shi, S.; Nuckolls, C.; Rickman, B. H. *J. Am. Chem. Soc.* **1997**, *119*, 10054.

(4) See footnote 8 in ref 3, and Fox, J. M.; Lin, D.; Itagaki, Y.; Fujita, T. *J. Org. Chem.* **1998**, *63*, 2031.

(5) Liu, L.; Katz, T. J. *Tetrahedron Lett.* **1990**, *31*, 3983.

(6) Nuckolls, C.; Katz, T. J.; Castellanos, L. *J. Am. Chem. Soc.* **1996**, *118*, 3767.

(7) Fox, J. M.; Goldberg, N. R.; Katz, T. J. *J. Org. Chem.* **1998**, *63*, 7456.

(8) (a) Martin, R. H.; Flammang-Barbieux, M.; Cosyn, J. P.; Gelbcke, M. *Tetrahedron Lett.* **1968**, 3507. (b) Martin, R. H.; Libert, V. *J. Chem. Res. Synop.* **1980**, 130, and ref 1 therein. (c) Moradpour, A.; Kagan, H.; Baes, M.; Morren, G.; Martin, R. H. *Tetrahedron* **1975**, *31*, 2139, and ref 12 therein.

(9) Yang, B.; Liu, L.; Katz, T. J.; Liberko, C. A.; Miller, L. L. *J. Am. Chem. Soc.* **1991**, *113*, 8993.

(10) Pereira, D. E.; Neelima; Leonard, N. J. *Tetrahedron* **1990**, *46*, 5895.

(11) Yang, B. V. Ph.D. Dissertation, Columbia University, 1987.

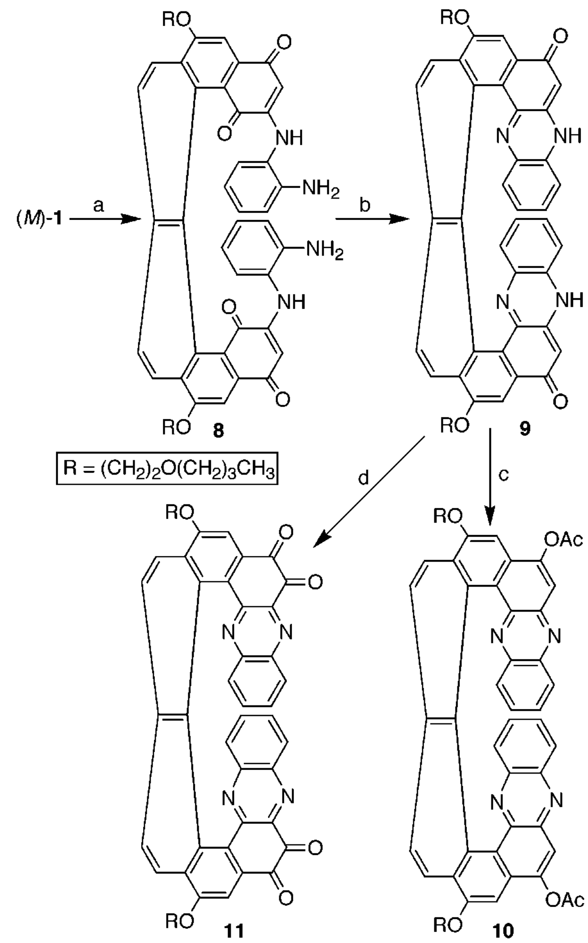
(12) Willmore, N. D. Ph.D. Dissertation, Columbia University, 1994.

(13) Dai, Y.; Katz, T. J. *J. Org. Chem.* **1997**, *62*, 1274.

(14) (a) Ott, R. *Monatsh. Chem.* **1959**, *90*, 827. (b) Ott, R.; Lachnit, R. *Monatsh. Chem.* **1973**, *104*, 15.

10.1021/jo9817570 CCC: $18.00

Scheme 1[a]



[a] Reaction conditions and yields: (a) 1,2-phenylenediamine, $Cu(OAc)_2$, 1:1 $MeOH-CH_2Cl_2$, 2.5 h (75% yield); (b) AcOH, reflux, 2.5 h; (c) Ac_2O, Et_3N, rt, 3 h (60% yield from **8**); (d) $Ph_2Se_2O_3$, THF, reflux, 2.5 h (60% yield from **8**).

and in its infrared absorption spectrum a peak at 1778 cm^{-1}, it must be the *O*-, not the *N*-, acetate of **9**.[17] That is, it has the phenol acetate structure. Accordingly, the differences between its UV−vis absorption spectrum and that of **9**, which has maxima at 490 and 580 nm (displayed in the Supporting Information),[15] and the presence of a carbonyl resonance in the ^{13}C NMR spectrum of **9**, at 168.7 ppm, show that **9** has the other structure, that of the vinylogous lactam.[18]

That 1,2-phenylenediamine, like secondary aliphatic amines,[3,12] adds to carbons 2 and 15 of bisquinone **1** is evidenced by the ^1H NMR spectrum of the adduct **10**, displaying a ^1H NMR for the acetate protons at the position at which aryl acetates normally resonate, ca. δ 2.3 ppm.[19] If instead the 1,2-phenylenediamine had added to carbons 3 and 14, the diacetate after the treatment with Ac_2O and Et_3N would have been **12**. Its acetates would have been positioned inside the helix, and therefore their protons should have resonated not at δ 2.3, but at ca. 1.1 ppm, where the acetates of **13** (δ 1.12)[6] and of one pair[20] of those of **14** (δ 1.01 ppm)[12] resonate.

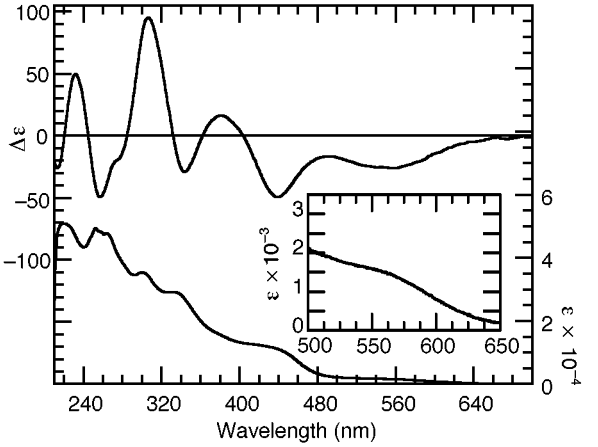
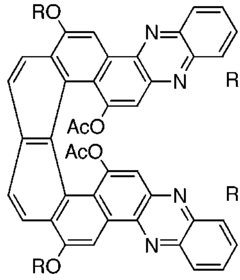
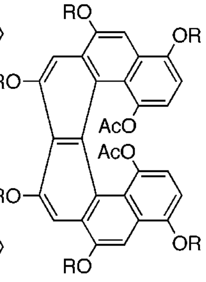


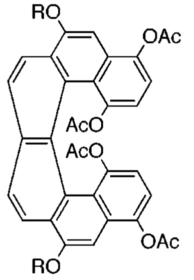
Figure 1. CD (upper curve, ordinate on left) and UV−vis absorption spectra (lower curve, ordinate on right) of a 2.0 × 10^{-5} M solution of (*M*)-(−)-**11** in CH_3CN.



R = $(CH_2)_2O(CH_2)_3CH_3$
12



R = $C_{12}H_{25}$
13



R = $(CH_2)_2O(CH_2)_3CH_3$
14

Although **9** could be isolated pure by crystallization from benzene−hexane, the yield was low (ca. 20%), for the mother liquor contained substantial amounts that could not be crystallized pure. Furthermore, **9** decomposed on silica gel or alumina, and therefore could not be purified by chromatography. However, as displayed in Scheme 1, benzeneseleninic anhydride[21] oxidizes **9** to bis-*o*-quinone **11**, and when the oxidation is carried out before **9** is purified, chromatography gives **11** in a yield (from **8**) of 59%. Orthoquinone **11** is a brown solid that melts at 220−221 °C, and it is soluble in CH_2Cl_2, $CHCl_3$, CH_3CN, benzene, THF, and acetone. The CD and UV−vis absorption spectra of its solutions in acetonitrile are displayed in Figure 1.

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[15] The UV−vis absorption spectra of both tautomers of **7**[16a] and of derivatives of 2-hydroxyphenazine[16b−d] have been assigned. The lactams show long wavelength absorption maxima at 479−517 nm, and the vinylogous lactam tautomer of **7** displays an additional maximum at ca. 550 nm. In the absorption spectra of the phenols and phenol acetates, the maxima at longest wavelengths are at 395−425 nm.[16]

[16] (a) Ružička, E.; Bekárek, V.; Kandrnál, J. *Collect. Czech. Chem. Commun.* **1975**, *40*, 1738. (b) Corbett, J. F. *Spectrochim. Acta* **1964**, *20*, 1665. (c) Badger, G. M.; Pearce, R. S.; Pettit, R. *J. Chem. Soc.* **1951**, 3204. (d) Albert, A.; Short, L. N. *J. Chem. Soc.* **1945**, 760.

[17] Similarly, **7** with Ac_2O/pyridine forms its *O*-acetate.[16a]

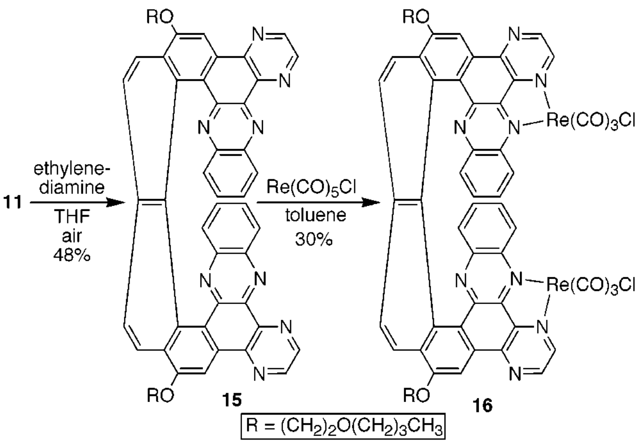
[18] The infrared spectrum of **9** in CCl_4 includes a peak at 1638 cm^{-1}, absent in the spectrum of **10** and approximately where phenazinones absorb.[16b] Ružička stated that because both tautomers of 5-hydroxybenzo[*a*]phenazines have a large number of absorbances between 1500 and 1650 cm^{-1}, it is impossible to assign the carbonyl stretch of the lactams.[16a] He noted that the only distinctive characteristic of a 5-hydroxybenzo[*a*]phenazine's lactam is an intense band at 1552 cm^{-1}, with shoulders at 1542 and 1520 cm^{-1}. Compound **9** shows peaks at 1572 and 1545 cm^{-1} that **10** does not.

[19] The acetate protons of phenyl acetate, β-naphthyl acetate, and α-naphthyl acetate resonate at 2.27, 2.31, and 2.41 ppm, respectively. See: *The Aldrich Library of ^{13}C and ^1H FT NMR Spectra*; Pouchert, C. J., Behnke, J., Eds.; Aldrich Chemical Co.: Milwaukee, WI, 1993.

[20] The other pair of **14**'s acetates resonate at δ 2.51 ppm.[12]

[21] Barton, D. H. R.; Finet, J.-P.; Thomas, M. *Tetrahedron* **1988**, *44*, 6397.

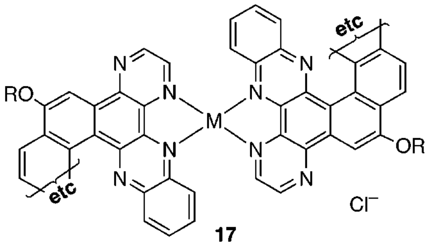
Scheme 2



The absorption maximum at 555 nm ($\epsilon = 1.5 \times 10^3$) is characteristic of *o*-quinones, which display peaks, assigned to n$-\pi^*$ transitions, between 500 and 580 nm (log ϵ ca. 1.4−1.8).[22] In the CD spectrum of **11** this absorption gives rise to a negatively dichroic peak, $\Delta\epsilon = -26$. Since the structure has *M*-helicity, it suggests that the n$-\pi^*$ transitions of (*M*)-helicenes that have *o*-quinone functions at outer rings, like those having *p*-quinones,[3] are negatively dichroic.

Preparation of a Helical Ligand. As shown in Scheme 2, ethylenediamine, a reagent that converts 9,10-phenanthrenequinone into dibenzo[*f*,*h*]quinoxaline,[23] also converts **11** into **15** in 48% yield. Since **15** is a derivative of the ligand 4,7-diaza-1,10-phenanthroline (pyrazino[2,3-*f*]quinoxaline),[24] we tried to complex it to metals, and as Scheme 2 also shows, it reacts with Re(CO)$_5$Cl in toluene[25] to give structure **16**, which was isolated in 30% yield. Other materials, presumably stereoisomers of **16**, were also formed, but these could not be obtained pure. Rhenium complex **16** is a red solid that does not melt at temperatures below 220 °C, and it is soluble in CH_2Cl_2, $CHCl_3$, toluene, and THF. Its ^{1}H NMR spectrum shows that its structure is symmetrical and its IR spectrum has the three absorptions required of the metal carbonyls[25] at 2023, 1926, and 1893 cm^{-1}.

To see whether ligand **15** would also make polymeric coordination complexes of structure **17**, and whether such polymers would display interesting optical properties, we treated **15** with CuCl in CH_2Cl_2—a combination that Pallenberg, Koenig, and Barnhart used to make hindered bis(2,9-dialkyl-1,10-phenanthroline)cuprous complexes.[26]



17

R = $(CH_2)_2O(CH_2)_3CH_3$

We obtained a material whose ^{1}H NMR spectrum is broad, as expected for the polymer, but its optical properties differ little from those of **15**. Its specific rotation, $[\alpha]_D$, is −4090 (*c* 0.014, 1:1 $CHCl_3-CH_3CN$) while that of **15** is −3860 (*c* 0.032, CH_2Cl_2), and none of the peaks in its CD spectrum are significantly larger than those in the spectrum of **15**. Given that the properties appeared unremarkable, we did not analyze whether structure **17** had failed to form or whether its tetrahedral metal center impedes conjugation between the helicene moieties. We note that polymers were not pursued of metals that, because they give square planar complexes, might be more likely to favor conjugation between ligands, for steric crowding is likely to distort structure **17** from a square planar geometry at the metal.[27,28]

Conclusions

Optically pure [8]helicene derivative **9** can easily be synthesized from nonracemic [6]helicenebisquinone **1** and 1,2-phenylenediamine. Orthoquinone **11** can be obtained by combining **9** with benzeneseleninic anhydride, and it reacts with ethylenediamine to form a helical bis-bidentate ligand. Like (*M*)-helicenes that have *p*-quinones on their outer rings, **11**, which instead has *o*-quinones, has a negative circular dichroism associated with its n$-\pi^*$ transition.

Experimental Section

THF and toluene were distilled from sodium-benzophenone ketyl, and CH_2Cl_2 and Et_3N from CaH_2. Benzeneseleninic anhydride was purchased from Acros. 1,2-Phenylenediamine, purchased from Aldrich, was recrystallized from toluene. Acetic anhydride (99.9%), copper acetate (98%), and ethylenediamine (99.5+%) were purchased from Aldrich and used without further purification. Glassware was flame-dried under vacuum and cooled under N_2, and unless otherwise stated, reactions were run under N_2. The matrix for FAB mass spectra was *m*-nitrobenzyl alcohol. Chromatography refers to “flash chromatography”.[29]

Reaction of (*M*)-1 with 1,2-Phenylenediamine. Preparation of 8. A mixture of (*M*)-(−)-**1**[3] (0.50 g, 0.81 mmol), 1,2-phenylenediamine (3.00 g, 27.8 mmol), and $Cu(OAc)_2$ (2.00 g, 11.0 mmol) in 1:1 CH_2Cl_2−methanol (120 mL) was refluxed in the air for 2.5 h. The mixture was cooled, and CH_2Cl_2 (ca. 400 mL) was added. The material, obtained by washing with 1 N HCl (3×) and with saturated aqueous $NaHCO_3$ (1×), drying (Na_2SO_4), and removing the solvent under reduced pressure, was dissolved in CH_2Cl_2 and chromatographed (eluting with 1:1 ethyl acetate−hexane). The yield of **8**, a red-brown solid, mp 127−128 °C, $[\alpha]_D$ −4230 (c 0.040, CH_2Cl_2), was 0.50 g (75%). IR (KBr): 3452, 3334, 2928, 2865, 1656, 1613, 1591 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.45 (d, 2H, J = 8.6 Hz), 7.95 (d, 2H, J =

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[22] Berger, S.; Rieker, A. In *The Chemistry of the Quinonoid Compounds*; Patai, S., Ed.; Wiley: London, 1974; Chapter 4.

[23] Mason, A. T. *J. Chem. Soc.* **1889**, *55*, 97.

[24] For metal complexes of 4,7-diaza-1,10-phenanthroline, see: (a) Karlsson, K.; Moucheron, C.; Kirsch-De Mesmaeker, A. *New J. Chem.* **1994**, *18*, 721, and ref 15 therein. (b) Real, J. A.; Muñoz, M. C.; Andrés, E.; Granier, T.; Gallois, B. *Inorg. Chem.* **1994**, *33*, 3587. (c) Didler, P.; Ortmans, I.; Kirsch-De Mesmaeker, A.; Watts, R. J. *Inorg. Chem.* **1993**, *32*, 5239, and refs 4 and 19 therein. (d) Didler, P.; Jacquet, L.; Kirsch-De Mesmaeker, A.; Hueber, R.; van Dorsselaer, A. *Inorg. Chem.* **1992**, *31*, 4803, and refs 9a and 15 therein. (e) Vogler, C.; Schwederski, B.; Klein, A.; Kaim, W. *J. Organomet. Chem.* **1992**, *436*, 367. (f) Masschelein, A.; Kirsch-De Mesmaeker, A.; Willsher, C. J.; Wilkinson, F. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 259, and ref 19 therein.

[25] Wrighton, M.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 998.

[26] Pallenberg, A. J.; Koenig, K. S.; Barnhart, D. M. *Inorg. Chem.* **1995**, *34*, 2833.

[27] For example, while the geometry at the metal in 2,2′-(dipyridyl)-$PdCl_2$ is square planar,[28a] the $PdCl_2$ complex of 6-methyl-2,2′-dipyridine, a ligand whose steric properties should be similar to those of **15**, is significantly distorted toward a tetrahedral geometry.[28b]

[28] (a) Canty, A. J.; Skelton, B. W.; Traill, P. R.; White, A. H. *Aust. J. Chem.* **1992**, *45*, 417. (b) Newkome, G. R.; Fronczek, F. R.; Gupta, V. K.; Puckett, W. E.; Pantaleo, D. C.; Kiefer, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 1782.

[29] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

8.6 Hz), 7.62 (s, 2H), 7.07 (dd, 2H, J = 7.4, 7.9 Hz), 7.00 (d, 2H, J = 7.6 Hz), 6.74 (m, 6H), 5.71 (s, 2H), 4.59 (m, 2H), 4.51 (m, 2H), 4.01 (m, 4H), 3.64 (t, 4H, J = 6.6 Hz), 3.60 (s, 4H), 1.64 (m, 4H), 1.44 (m, 4H), 0.96 (t, 6H, J = 7.2 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 183.3, 180.6, 159.3, 147.5, 141.7, 136.0, 132.7, 131.6, 127.9, 127.4, 126.4, 125.7, 125.3, 124.5, 122.3, 122.0, 118.6, 116.6, 102.6, 100.4, 71.2, 68.7, 68.6, 31.6, 19.1, 13.8 ppm. HRMS (FAB): calcd for $C_{50}H_{49}N_4O_8$ (M + 1) 833.3550, found 833.3541.

Preparation of 9. Compound **8** (0.50 g, 0.60 mmol) was refluxed for 2.5 h in acetic acid (75 mL). After cooling to room temperature, the red solution was poured into CH_2Cl_2 (400 mL), washed twice with water and twice with saturated aqueous $NaHCO_3$, and dried (Na_2SO_4). The solvents were removed to yield 0.49 g of a dark red solid, which was used directly in the next step. A sample for analysis was crystallized from benzene−hexane. Mp > 220 °C. $[\alpha]_D$ −4520 (*c* 0.040, CH_2Cl_2). IR (CCl_4): 2960, 2931, 2859, 1741, 1709, 1638, 1621, 1598 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.62 (d, 2H, J = 8.5 Hz), 8.21 (d, 2H, J = 8.5 Hz), 7.60 (d, 2H, J = 8.3 Hz), 7.48 (dd, 2H, J = 7.2, 8.2 Hz), 7.34 (dd, 2H, J = 7.5, 7.3), 7.13 (d, 2H, J = 8.2 Hz), 6.96 (s, 2H), 6.46 (s, 2H), 4.34 (m, 4H), 4.07 (m, 4H), 3.76 (m, 4H), 1.74 (m, 4H), 1.53 (m, 6H, CH_2 + NH), 1.02 (t, 6H, J = 7.4 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.7, 156.9, 140.5, 140.2, 136.9, 133.3, 132,0, 131.3, 130.9, 130.0, 129.5, 128.4, 127.6, 126.7, 125.3, 122.3, 120.8, 120.1, 99.8, 97.8, 71.6, 69.1, 68.6, 32.0, 19.4, 14.0 ppm. HRMS (FAB): calcd for $C_{50}H_{45}N_4O_6$ (M + 1) 797.3339, found 797.3355.

Preparation of Diacetate 10. Triethylamine (0.7 mL, 5 mmol) was added to a solution of crude **9** (0.120 g) in acetic anhydride (7.0 mL, 74 mmol). After this had stirred at room temperature for 3 h, the solvents were removed under reduced pressure, and the residue was chromatographed (eluting first with 15% acetone−85% CH_2Cl_2 and then with 20% acetone−80% CH_2Cl_2) to give 0.082 g (62%) of **10**, a yellow solid, mp 207−208 °C. IR (CCl_4): 2929, 2856, 1778, 1741, 1705, 1599 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, 2H, J = 7.9 Hz), 8.17 (d, 2H, J = 8.6 Hz), 8.06 (d, 2H, J = 8.5 Hz), 7.69 (m, 2H), 7.51 (m, 2H), 7.30 (s, 2H), 7.15 (d, 2H, J = 8.5 Hz), 6.25 (s, 2H), 4.26 (m, 4H), 4.07 (m, 4H), 3.76 (m, 4H), 2.30 (s, 6H), 1.73 (m, 4H), 1.52 (m, 4H), 1.01 (t, 6H, J = 7.4 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.3, 156.3, 147.8, 141.3, 141.0, 139.8, 137.9, 132.1, 129.6, 129.3, 128.8, 128.7, 128.1, 127.9, 127.7 (2 peaks), 126.1, 122.1, 120.8, 117.1, 97.3, 71.7, 69.0, 68.2, 31.9, 20.9, 19.4, 14.0 ppm. HRMS (FAB): calcd for $C_{50}H_{48}N_4O_8$ 880.3472, found 880.3440.

Preparation of Bis-*o*-quinone 11. A mixture of crude **9** (0.49 g) and benzeneseleninic anhydride (1.96 g, 5.44 mmol) in THF (50 mL) was refluxed for 2.5 h. The reaction mixture was cooled, and CH_2Cl_2 was added. The solution was washed twice with saturated aqueous $NaHCO_3$ and once with H_2O and dried (Na_2SO_4). The solvents were removed under reduced pressure, and the residue was triturated with hexane. Chromatography with 1:1 ethyl acetate−CH_2Cl_2 gave 0.29 g (59% for the 2 steps) of **11**, a brown solid, mp 220−221 °C, $[\alpha]_D$ −7400 (*c* 0.005, CH_2Cl_2); −7700 (*c* 0.005, CH_3CN); −9050 (*c* 0.005, THF); −11560 (*c* 0.005, C_6H_6).[30] IR (KBr): 2930, 2869, 1722, 1678, 1593, 1511 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.52 (d, 2H, J = 8.5 Hz), 8.21 (d, 2H, J = 8.5 Hz), 8.17 (d, 2H, J = 8.4 Hz), 7.69 (dd, 2H, J = 7.5, 7.9 Hz), 7.53 (dd, 2H, J = 7.4, 7.2), 6.88 (d, 2H, J = 8.3), 6.76 (s, 2H), 4.25 (m, 2H), 4.07 (m, 2H), 3.97 (m, 4H), 3.68 (t, 4H, J = 6.6 Hz), 1.70 (m, 4H), 1.49 (m, 4H), 1.00 (t, 6H, J = 7.4 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 177.8, 177.0, 157.0, 148.3, 141.2, 140.5, 139.8, 132.5, 132.2, 131.4, 131.0, 130.5, 130.3, 130.1, 129.4, 128.9, 128.4, 127.5, 121.5, 102.7, 71.5, 69.0, 68.7, 31.8, 19.4, 14.0 ppm. HRMS (FAB): calcd for $C_{50}H_{43}N_4O_8$ (M + 3)[31] 827.3081, found 827.3062. Anal. Calcd for $C_{50}H_{40}N_4O_8$: C, 72.8; H, 4.9; N, 6.8. Found: C, 72.3; H, 5.0; N, 6.4.

Preparation of 15. Ethylenediamine (0.36 mL, 0.32 g, 5.4 mmol) was added to a solution of **11** (0.100 g, 0.121 mmol) in THF (15 mL). After the mixture had refluxed in the air for 3 h, the solvent was stripped, and the residue was filtered through a plug of silica gel (2 in. × 0.5 in., eluting with 1:1 MeOH−acetone). The filtrate was concentrated, and the residue, dissolved in CH_2Cl_2, was chromatographed (eluting with 20% MeOH−80% acetone). The yield of **15**, a yellow solid, mp > 220 °C, $[\alpha]_D$ −3860 (*c* 0.032, CH_2Cl_2), was 0.052 g (48%). IR (KBr): 3048, 2926, 2863, 1594, 1529, 1508 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.04 (d, 2H, J = 2.0 Hz), 8.78 (d, 2H, J = 2.0 Hz), 8.59 (d, 2H, J = 8.6 Hz), 8.21 (d, 2H, J = 8.6 Hz), 7.97 (d, 2H, J = 8.4 Hz), 7.72 (dd, 2H, J = 7.8, 7.3 Hz), 7.58 (dd, 2H, J = 8.1, 7.0 Hz), 7.40 (s, 2H), 7.15 (d, 2H, J = 8.4 Hz), 4.34 (m, 4H), 4.07 (m, 4H), 3.76 (m, 4H), 1.73 (m, 4H), 1.54 (m, 4H), 1.02 (t, 6H, J = 7.3 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.7, 144.7, 144.5, 142.9, 141.1, 140.7, 140.5, 140.3, 138.6, 131.8, 131.0, 129.8−129.5 (m), 129.0, 127.5, 127.0, 121.7, 120.9, 99.5, 71.6, 69.1, 68.5, 32.0, 19.5, 14.0 ppm. HRMS: calcd for $C_{54}H_{45}N_8O_4$ (M + 1) 869.3564, found 869.3553.

Reaction of 15 with $Re(CO)_5Cl$. Preparation of 16. A solution of **15** (7 mg, 8 μmol) and $Re(CO)_5Cl$ (6 mg, 17 μmol) in 1 mL of toluene was refluxed for 12 h. After the solvent had been removed, preparative TLC on alumina (eluant 20% ethyl acetate in benzene) separated two red materials. The one with the smaller R_f was **16** (4 mg, 33% yield), a red solid, mp > 220 °C, $[\alpha]_D$ −3400 (*c* 0.066, CH_2Cl_2). IR (KBr): 2928, 2865, 2023, 1926, 1893, 1594, 1508, 1479 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.97 (d, 2H, J = 2.7 Hz), 8.92 (d, 2H, J = 2.6 Hz), 8.76 (d, 2H, J = 8.5 Hz), 8.45 (d, 2H, J = 8.8 Hz), 8.35 (d, 2H, J = 8.5 Hz), 8.02 (m, 2H), 7.85 (m, 2H), 7.59 (s, 2H), 7.30 (d, 2H, J = 8.5 Hz), 4.45 (m, 4H), 4.13 (m, 4H), 3.78 (m, 4H), 1.76 (m, 4H), 1.56 (m, 4H), 1.02 (t, 6H, J = 7.4 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.3, 148.0, 145.8, 142.8, 142.1, 141.0, 139.0, 138.9, 133.7, 133.0, 131.9, 130.7−129.4 (m), 128.5, 127.9, 127.3, 121.8, 121.0, 100.4, 71.7, 69.2, 68.9, 31.9, 19.4, 14.0 ppm. HRMS (FAB): calcd for $C_{60}H_{44}Cl_2N_8O_{10}Re_2$ 1480.1670, found 1480.1700.

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Supporting Information Available: ^{1}H NMR, ^{13}C NMR, and IR spectra of **8**−**11**, **15**, and **16**; UV−vis absorption spectra of **9**−**11**, **15**, and **16**; and CD spectra of **11**, **15**, and **16** (22 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(30) The changes in the specific rotation of **9** when the solvent is varied are accompanied by changes in the CD spectrum. The peak at longest wavelength in the CD spectrum of 2.0 × 10^{-5} M solutions of **9** is at 566 nm when the solvent is CH_2Cl_2, 560 nm when it is CH_3CN, 544 nm when it is benzene, and 527 nm when it is THF. The spectra are displayed in the Supporting Information.

(31) M + 2 peaks are frequently observed in the mass spectra of *o*-quinones. Thus, the observed peak in the mass spectrum of **9** corresponds to (M + 2) + 1. See Zeller, K.-P. In *The Chemistry of the Quinonoid Compounds*; Patai, S., Ed.; Wiley: London, 1974; Chapter 5.