plexes and extended networks can be envisaged to elaborate new supramolecular magnetic materials (high-spin molecules and molecular-based magnets).

Experimental Section

H_4[**1**]: The proligand was prepared in a standard manner[18] from the condensation of 1,3-phenylenediamine and ethyl oxalyl chloride in THF, and was isolated as the diethyl ester derivative (90%). Elemental analysis calcd (%) for $C_{14}H_{16}N_2O_6$ (308): C 54.55, H 5.19, N 9.09; found: C 54.57, H 5.18, N 9.04; ^{1}H NMR ([D$_6$]DMSO): $\delta = 1.32$ (t, 6H; $2CH_3$), 4.31 (q, 4H; $2CH_2O$), 7.34 (dt, 1H; 5-H of $C_6H_4N_2$), 7.50 (dd, 2H; 4-H and 6-H of $C_6H_4N_2$), 8.22 (t, 1H; 2-H of $C_6H_4N_2$), 10.83 (s, 2H; 2NH); ^{13}C NMR ([D$_6$]DMSO): $\delta = 14.17$ ($2CH_3$), 62.71 ($2CH_2O$), 113.25 (2-C of $C_6H_4N_2$), 117.45 (4-C and 6-C of $C_6H_4N_2$), 129.34 (5-C of $C_6H_4N_2$), 138.08 (1-C and 3-C of $C_6H_4N_2$), 156.13 (2-C(O)NH), 161.02 ($2CO_2$); IR (KBr): $\tilde{\nu} = 3349$ (N–H), 2979, 2943 (C–H), 1725, 1715, 1698 cm^{-1} (C=O); UV/Vis (THF): λ_{max} (ε) = 335 nm (800).

Complex **2** was obtained following a reported procedure[18] by reaction of the diethyl ester derivative of the ligand with Cu^{2+} ions in basic aqueous media, and isolated as its octahydrate sodium salt (85%). Elemental analysis calcd (%) for $C_{20}H_{24}Cu_2N_4Na_4O_{20}$ (859): C 27.94, H 2.79, N 6.52; found: C 27.77, H 2.62, N 6.40; IR (KBr): $\tilde{\nu} = 3423$ (O–H), 1659, 1597 cm^{-1} (C=O); UV/Vis (H_2O): λ_{max} (ε) = 645 (150), 380 sh (1600), 345 nm (2650). Crystals of **2**, well-formed small dark green prisms, suitable for X-ray diffraction were obtained by slow vapor diffusion of methanol into concentrated aqueous solutions of **2** at 5 °C.

Crystal data for **2**: $C_{20}H_{28}Cu_2N_4Na_4O_{22}$, $M_r = 895.50$, triclinic, space group $P\bar{1}$, $a = 11.1489(15)$, $b = 12.8545(9)$, $c = 13.3454(19)$ Å, $\alpha = 63.855(8)$, $\beta = 78.305(12)$, $\gamma = 68.695(10)°$, $V = 1597.5(3)$ Å^3, $T = 293$ K, $Z = 2$, $\rho_{calcd} = 1.862$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 1.485$ mm^{-1}. Lorentz and polarization effects and absorption correction. 5579 unique reflections, and 3616 observed with $I > 2\sigma(I)$. The structure was solved by direct methods using SHELXS 97, and refined by the full-matrix least-squares method on F^2 using SHELXL 97. The hydrogen atoms from the organic ligand were located from a difference synthesis and refined with an overall isotropic thermal parameter, while those from the water molecules were not found or calculated. Refinement of 471 variables with anisotropic thermal parameters for all non-hydrogen atoms gave $R = 0.0503$ and $R_w = 0.112$, with $S = 0.97$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-157314. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Received: February 16, 2001 [Z16620]

[1] O. Kahn, *Molecular Magnetism*, VCH, New York, **1993**.

[2] a) O. Kahn, *Angew. Chem.* **1985**, *97*, 837; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 834; b) O. Kahn, *Adv. Inorg. Chem.* **1995**, *43*, 179.

[3] a) O. Kahn, *Acc. Chem. Res.* **1993**, *26*, 259; b) J. S. Miller, A. J. Epstein, *Angew. Chem.* **1994**, *106*, 399; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 385.

[4] S. Mitsubori, T. Ishida, T. Nogami, H. Iwamura, *Chem. Lett.* **1994**, 285; H. Oshio, H. Ichida, *J. Phys. Chem.* **1995**, *99*, 3294; A. M. W. Cargill-Thompson, D. Gatteschi, J. A. McCleverty, J. A. Navas, E. Rentschler, M. D. Ward, *Inorg. Chem.* **1996**, *35*, 2701; F. Lloret, G. De Munno, M. Julve, J. Cano, R. Ruiz, A. Caneschi, *Angew. Chem.* **1998**, *110*, 143; *Angew. Chem. Int. Ed.* **1998**, *37*, 135.

[5] a) D. A. Dougherty, *Acc. Chem. Res.* **1991**, *24*, 88; b) H. Iwamura, N. Koga, *Acc. Chem. Res.* **1993**, *26*, 346; c) A. Rajca, *Chem. Rev.* **1994**, *94*, 871.

[6] R. Ruiz, J. Faus, F. Lloret, M. Julve, Y. Journaux, *Coord. Chem. Rev.* **1999**, *193–195*, 1069.

[7] A. Aukauloo, X. Ottenwaelder, R. Ruiz, S. Poussereau, Y. Pei, Y. Journaux, P. Fleurat, F. Volatron, B. Cervera, M. C. Muñoz, *Eur. J. Inorg. Chem.* **1999**, 1067; A. Aukauloo, X. Ottenwaelder, R. Ruiz, Y. Journaux, Y. Pei, E. Rivière, M. C. Muñoz, *Eur. J. Inorg. Chem.* **2000**, 951.

[8] S. Rajca, A. Rajca, *J. Am. Chem. Soc.* **1995**, *117*, 9172, and refs therein.

[9] Computational details: The methodology used to evaluate the coupling exchange constants is described elsewhere.[10] We carried out the calculations using the hybrid B3LYP method[11] as implemented in GAUSSIAN98, with the all-electron double-basis proposed by Ahlrichs and co-workers, except for the metal atom where we have used a triple-basis and two p polarization functions.[12]

[10] E. Ruiz, P. Alemany, S. Alvarez, J. Cano, *J. Am. Chem. Soc.* **1997**, *119*, 1297; E. Ruiz, J. Cano, S. Alvarez, P. Alemany, *J. Comput. Chem.* **1999**, *20*, 1391.

[11] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.

[12] a) A. Schaefer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571; b) A. Schaefer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829.

[13] R. S. Mulliken, *J. Chem. Phys.* **1962**, *36*, 3428.

[14] a) P. J. Stang, B. Olenyuk, *Acc. Chem. Res.* **1997**, *30*, 502; b) G. F. Swiegers, T. J. Malefetse, *Chem. Rev.* **2000**, *100*, 3483.

[15] A. Jouaiti, M. Loï, M. W. Hosseini, A. D. Cian, *Chem. Commun.* **2000**, 2085.

[16] M. A. Aebersold, M. Gillon, O. Plantevin, L. Pardi, O. Kahn, P. Bergerat, I. F. T. von Seggern, L. Öhrström, A. Grand, E. Lelièvre-Berna, *J. Am. Chem. Soc.* **1998**, *120*, 5238.

[17] O. Kahn, *Acc. Chem. Res.* **2000**, *33*, 647.

[18] B. Cervera, J. L. Sanz, M. J. Ibáñez, G. Vila, F. Lloret, M. Julve, R. Ruiz, X. Ottenwaelder, A. Aukauloo, S. Poussereau, Y. Journaux, M. C. Muñoz, *J. Chem. Soc. Dalton Trans.* **1998**, 781.

Conjugated Complexes Composed of Quinonediimine and Palladium: Controlled Formation of a Conjugated Trimetallic Macrocycle**

Toshiyuki Moriuchi, Manabu Miyaishi, and Toshikazu Hirao*

π-Conjugated polymers have attracted much attention for application as electrical materials owing to their electrical properties.[1] The properties of π-conjugated polymers are considered to be modified drastically by the incorporation of metal atoms.[2, 3] Conjugated polymeric complexes in which transition metals are incorporated in the main chain represent one approach.[3] Most of the interest in these conjugated polymeric complexes has been concerned with the nature of the interactions between metal centers through a π-conjugated chain. Transition metal directed assembly is regarded as

[*] Prof. Dr. T. Hirao, Dr. T. Moriuchi, M. Miyaishi
Department of Applied Chemistry
Faculty of Engineering, Osaka University
Yamada-oka, Suita, Osaka 565-0871 (Japan)
Fax: (+81) 6-6879-7415
E-mail: hirao@ap.chem.eng.osaka-u.ac.jp

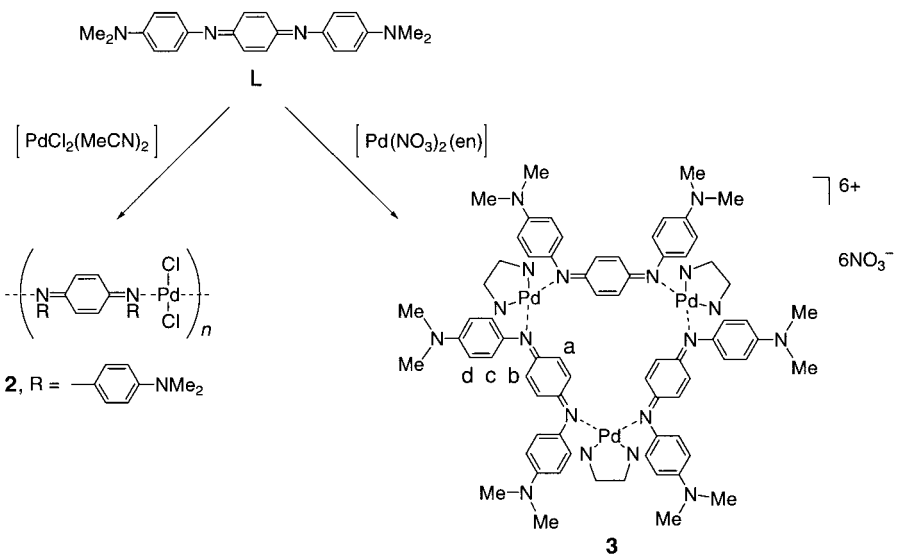
[**] This work was financially supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan. We thank Professor R. Arakawa at Kansai University for the ESI-MS measurements. Thanks are also due to the Analytical Center, Faculty of Engineering, Osaka University for the use of their facilities.

Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

  1433-7851/01/4016-3042 $ 17.50+.50/0

a useful approach to an architecturally controlled formation of conjugated polymeric or macrocyclic complexes with π-conjugated ligands.[4] We have already demonstrated that the redox-active π-conjugated ligand *N*,*N*′-bis(4-dimethylaminophenyl)-1,4-benzoquinonediimine (L) serves as a bridging ligand to afford the conjugated homobimetallic palladium(II) complex [L′PdLPdL′] (**1**) with the palladium(II) complex bearing the N-heterocyclic tridentate podand ligand *N*,*N*′-bis(2-phenylethyl)-2,6-pyridinedicarboxamide (L′).[5] Complex **1** is present as a mixture of *syn* and *anti* isomers in dichloromethane. An array of L with a palladium complex having two coordination sites was expected to give a conjugated polymeric or macrocyclic complex. In fact, control of the coordination mode of the quinonediimine moiety of L allowed the formation of a conjugated trimetallic macrocycle.

Treatment of L with $[PdCl_2(MeCN)_2]$ in acetonitrile led to the formation of the conjugated polymeric complex **2**, in which palladium centers are incorporated in the main chain (Scheme 1). The electronic spectrum of **2** in DMSO exhibited



Scheme 1. Reaction of L with $[PdCl_2(MeCN)_2]$ and $[Pd(NO_3)_2(en)]$.

a strong, broad absorption around 600 – 1000 nm, probably assignable to a low-energy charge-transfer transition with significant contribution from palladium; this indicates the coordination of the quinonediimine nitrogen atoms to palladium centers.[5] The broad absorption band supports the formation of the conjugated polymeric complex **2**.[6] In **2**, both *syn* and *anti* configuration of the quinonediimine moieties appear to be present.

To regulate the coordination mode of the quinonediimine moiety, a metal-directed strategy for the construction of metallomacrocycles was embarked upon by using $[Pd(NO_3)_2(en)]$ which has *cis* binding sites as a "metal clip". The conjugated trimetallic macrocycle $[\{Pd(en)(L)\}_3](NO_3)_6$ (**3**) was obtained quantitatively by treating L with an equimolar amount of $[Pd(NO_3)_2(en)]$ (Scheme 1). The formation of the trimetallic macrocycle **3** was elucidated from spectral data. Only one well-resolved signal for each type of proton was observed in the downfield region of the ^{1}H NMR spectrum (Figure 1); this indicates the formation of a symmetrical macrocycle. Furthermore, the H_a and H_b protons of the quinonediimine moiety were observed as singlet, which suggests the *syn* configuration. No other products were

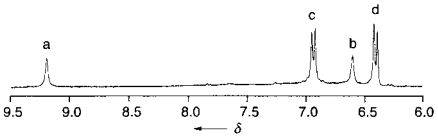


Figure 1. Downfield region of the ^{1}H NMR spectrum of **3**. For details see text.

detected. The ESI-MS spectrum also supported the formation of **3** (*m*/*z* 255.3 $[M-6NO_3]^{6+}$, 318.4 $[M-5NO_3]^{5+}$, 414.0 $[M-4NO_3]^{4+}$, 573.9 $[M-3NO_3]^{3+}$, 890.9 $[M-2NO_3]^{2+}$; Figure 2). The electronic spectrum of **3** in MeOH exhibited a strong, broad absorption band around 800 nm (Figure 3), probably assignable to a low-energy charge-transfer transition with significant contribution from palladium owing to the coordination of the quinonediimine nitrogen atoms to palladium centers.

Further structural information on **3** was obtained by X-ray crystallography.[7] The solid-state molecular structure of **3** confirmed a trimetallic macrocyclic skeleton and the coordination of both quinonediimine nitrogen atoms to the palladium centers in the *syn* configuration with a Pd–Pd distance of 7.68 Å (Figure 4). The molecule sits on an inversion center. The most noteworthy structural feature is that the quinonediimine planes are inclined at about 28° to the plane defined by the six nitrogen atoms of the quinonediimine moieties. An open cavity with different faces is formed, which is

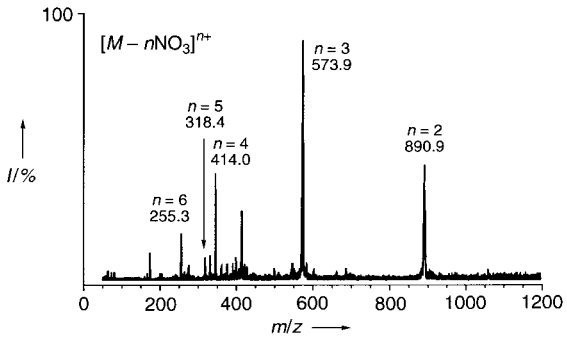


Figure 2. ESI-MS spectrum of **3**. *I* = intensity.

reminiscent of the cone conformation of calixarenes. This inclination of the quinonediimine planes is probably due to the coordination of the nitrogen atoms to the palladium centers, which results in ideal bite angles at Pd (N_{qd}-Pd-$N_{qd'}$ 91.2, 91.3°). The top and bottom sizes of the cavity, defined as

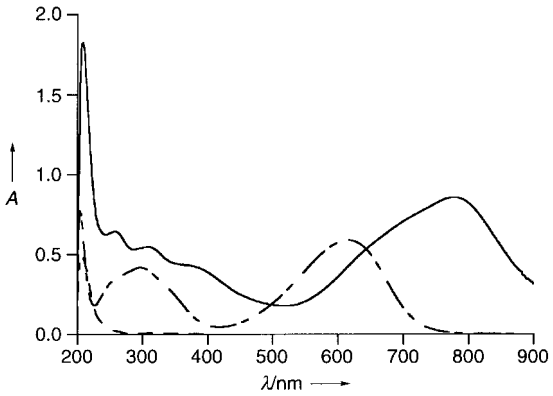


Figure 3. Electronic spectra of $[Pd(NO_3)_2(en)]$ (----), L (•–•–), and **3** (——); 2.0×10^{-5} M in MeOH. A = absorbance.

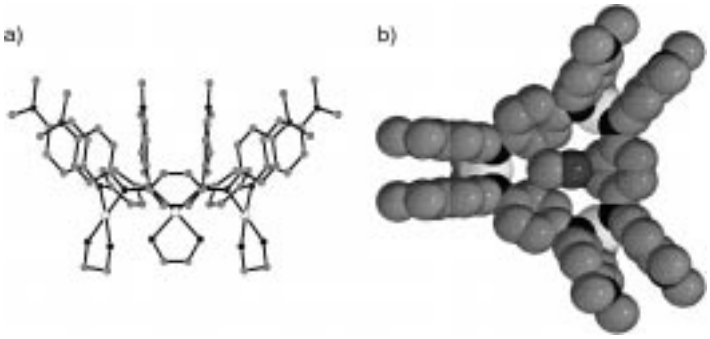


Figure 4. a) Molecular structure of **3** (H atoms, NO_3^- ions, and MeOH molecules omitted for clarity). b) Space-filling representation of the molecular structure of **3** (H atoms and NO_3^- ions omitted for clarity). Two MeOH molecules are located at the top and bottom of the cavity.

the distance between C_a and $C_{a'}$ and between C_b and $C_{b'}$, are 3.66 and 6.72 Å, respectively (Figure 5). Due to π conjugation of L, the orientation of each phenylene ring should be nearly parallel to the quinonediimine plane. The steric interaction between the hydrogen atoms H_b and H_c, however, requires rotation of the phenylene ring of L away from this orientation, and results in dihedral angles of 43.2, 45.4, and 53.3° between the phenylene and quinonediimine planes (Figure 5). Another remarkable feature of the structure is the orientation of the phenylene rings of L in a face-to-face arrangement at a

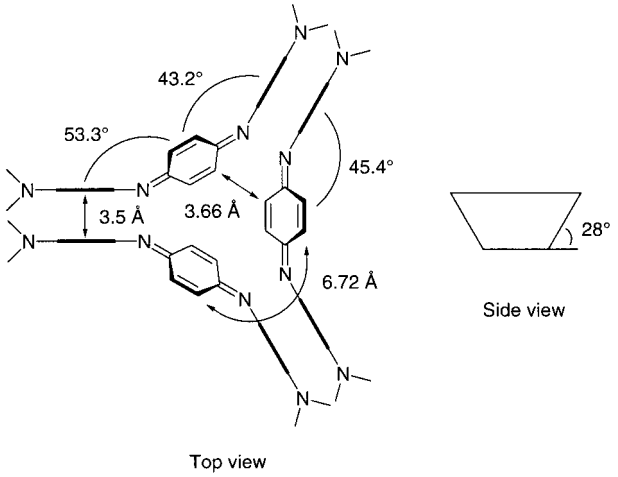


Figure 5. Schematic representation of **3**.

distance of about 3.5 Å at each corner of the triangle, which suggests a π–π stacking interaction. In addition to *cis* binding to [Pd(en)] units this π–π stacking interaction may partly contribute to the preferential formation of the trimetallic macrocycle over polymeric complexes. Architectural control of well-arranged metallomacrocycles based on transition metal directed assembly is a current research area in metal-directed chemistry.[4, 8, 9] Considerable attention has been focused on the construction of a variety of metallosquares,[4, 8] while metallotriangles have remained relatively unexplored.[4c–e, 8h,m,o, 9] The angular strain at the metal center and the ligand flexibility resulted in the selective formation of the metallotriangle **3**.

Macrocycle **3** accommodates two MeOH molecules at the top and bottom of the cavity. This indicates the capability to encapsulate guest molecules. A preliminary experiment on guest binding in D_2O showed that the association constant for 1,2-dimethoxybenzene, calculated from ^{1}H NMR spectroscopic data, was $4.0 \times 10^3\ M^{-1}$.

In conclusion, an alternative coordination array of the redox-active π-conjugated bridging quinonediimine spacer L and a palladium unit led to the formation of the conjugated polymeric complex **2** or the conjugated trimetallic macrocycle **3**. In the latter case, the complexation is architecturally controlled by *cis* binding to [Pd(en)] fragments to give a trimetallic macrocycle with a cone conformation. A π–π stacking interaction between the phenylene rings of L may stabilize the triangular complex. An open cavity appears to offer a binding site for guest molecules. The present conjugated complexes are regarded as potential redox-active systems, which might be applied as catalysts and electronic materials. Further investigation, including redox and recognition properties of the trimetallic macrocycle **3**, is now in progress.

Experimental Section

3: A mixture of L (69.0 mg, 0.20 mmol) and $[Pd(NO_3)_2(en)]$ (58.1 mg, 0.20 mmol) was stirred in acetonitrile (20 mL) under argon at room temperature for 2 h. After evaporation of the solvent, compound **3** was isolated in 92% yield by recrystallization from methanol. ^{1}H NMR (400 MHz, D_2O): $\delta = 9.17$ (s, 6H), 6.91 (d, $J = 8.7$ Hz, 12H), 6.58 (s, 6H), 6.37 (d, $J = 8.7$ Hz, 12H), 3.01–2.95 (m, 6H), 2.94–2.88 (m, 6H), 2.90 (s, 36H); ^{13}C NMR (100 MHz, D_2O): $\delta = 158.1, 151.7, 136.9, 134.5, 129.2, 127.1, 112.6, 47.0, 39.7$; ESI-MS: see Figure 2.

Received: March 29, 2001 [Z16868]

[1] a) A. G. MacDiarmid, L. S. Yang, W. S. Huang, B. D. Humphrey, *Synth. Met.* **1987**, *18*, 393; b) W. R. Salaneck, D. T. Clark, E. J. Samuelsen, *Science and Application of Conductive Polymers*, Adams Hilger, New York, **1990**; c) D. Ofer, R. M. Crooks, M. S. Wrighton, *J. Am. Chem. Soc.* **1990**, *112*, 7869; d) G. Gustafsson, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri, A. J. Heeger, *Nature* **1992**, *357*, 477; e) D. D. C. Bradley, *Synth. Met.* **1993**, *54*, 401; f) J. S. Miller, *Adv. Mater.* **1993**, *5*, 587; J. S. Miller, *Adv. Mater.* **1993**, *5*, 671; g) D. Bloor, *Chem. Br.* **1995**, *31*, 385; h) I. Jestin, P. Frère, P. Blanchard, J. Roncali, *Angew. Chem.* **1998**, *110*, 990; *Angew. Chem. Int. Ed.* **1998**, *37*, 942, and references therein. See also the Nobel lectures of Heeger, MacDiarmid, and Shirakawa in *Angew. Chem./Angew. Chem. Int. Ed.* **2001**, issue 14.

[2] a) R. Ramaraj, P. Natarajan, *J. Polym. Sci. A* **1991**, *29*, 1339; b) T. Yamamoto, Y. Yoneda, T. Maruyama, *J. Chem. Soc. Chem. Commun.*

  1433-7851/01/4016-3044 $ 17.50+.50/0

1992, 1652; c) T. Hirao, M. Higuchi, I. Ikeda, Y. Ohshiro, *J. Chem. Soc. Chem. Commun.* **1993**, 194; d) T. Hirao, M. Higuchi, B. Hatano, I. Ikeda, *Tetrahedron Lett.* **1995**, *36*, 5925; e) M. Higuchi, S. Yamaguchi, T. Hirao, *Synlett* **1996**, 1213; f) M. Higuchi, D. Imoda, T. Hirao, *Macromolecules* **1996**, *29*, 8277; g) M. Higuchi, I. Ikeda, T. Hirao, *J. Org. Chem.* **1997**, *62*, 1072; h) T. Hirao, S. Yamaguchi, S. Fukuhara, *Tetrahedron Lett.* **1999**, *40*, 3009; i) R. W. Murray in *Electroanalytical Chemistry, Vol. 13* (Ed.: A. J. Bard), Marcel Dekker, New York, **1984**, p. 191; j) H. D. Abruna in *Electroresponsive Molecular and Polymer System, Vol. 1* (Ed.: T. A. Skotheim), Marcel Dekker, New York, **1988**, p. 97.

[3] a) K. Sonogashira, S. Takahashi, N. Hagihara, *Macromolecules* **1977**, *10*, 879; b) M. Hmyene, A. Yassar, M. Escorne, A. Percheron-Guegan, F. Garnier, *Adv. Mater.* **1994**, *6*, 564; c) M. Altmann, U. H. F. Bunz, *Angew. Chem.* **1995**, *107*, 603; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 569; d) O. Lavastre, M. Even, P. H. Dixneuf, A. Pacreau, J.-P. Vairon, *Organometallics* **1996**, *15*, 1530; e) J. B. Sheridan, A. J. Lough, I. Manners, *Organometallics* **1996**, *15*, 2195; f) T. Hirao, M. Kurashina, K. Aramaki, H. Nishihara, *J. Chem. Soc. Dalton Trans.* **1996**, 2929; g) P. Nguyen, P. Gómez-Elipe, I. Manners, *Chem. Rev.* **1999**, *99*, 1515, and references therein; h) F. Würthner, A. Sautter, C. Thalacker, *Angew. Chem.* **2000**, *112*, 1298; *Angew. Chem. Int. Ed.* **2000**, *39*, 1243.

[4] For reviews, see a) P. J. Stang, B. Olenyuk, *Acc. Chem. Res.* **1997**, *30*, 502; b) R. V. Slone, K. D. Benkstein, S. Bélanger, J. T. Hupp, I. A. Guzei, A. L. Rheingold, *Coord. Chem. Rev.* **1998**, *171*, 221; c) B. Olenyuk, A. Fechtenkötter, P. J. Stang, *J. Chem. Soc. Dalton Trans.* **1998**, 1707; d) S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853; e) G. F. Swiegers, T. J. Malefetse, *Chem. Rev.* **2000**, *100*, 3483; f) M. Fujita, K. Umemoto, M. Yoshizawa, N. Fujita, T. Kusukawa, K. Biradha, *Chem. Commun.* **2001**, 509, and references therein.

[5] T. Moriuchi, S. Bandoh, M. Miyaishi, T. Hirao, *Eur. J. Inorg. Chem.* **2001**, 651.

[6] The distinct signal broading observed by NMR spectroscopy during the titration of L with $[PdCl_2(MeCN)_2]$ indicated the formation of a conjugated polymeric complex. We have also demonstrated that the controlled complexation of the emeraldine base of poly(*o*-toluidine) with Pd^{II} compounds in an organic solvent affords cross-linked conjugated polymeric complexes.[2h]

[7] Crystal data for **3**: $C_{72}H_{96}N_{24}O_{18}Pd_3 \cdot 2CH_3OH$, $M_r = 1968.98$, orthorhombic, space group *Pnma* (no. 62), $a = 27.6315(9)$, $b = 22.1045(7)$, $c = 17.7133(6)$ Å, $V = 10\,818.9(6)$ Å^3, $Z = 4$, $T = 23.0\,^\circ C$, $\rho_{calcd} = 1.209$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 5.59$ cm^{-1}, $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å), $R = 0.090$, $R_w = 0.253$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-160516. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[8] a) M. Fujita, J. Yazaki, K. Ogura, *J. Am. Chem. Soc.* **1990**, *112*, 5645; b) H. Rauter, E. C. Hillgeris, B. Lippert, *J. Chem. Soc. Chem. Commun.* **1992**, 1385; c) T. Kajiwara, T. Ito, *J. Chem. Soc. Chem. Commun.* **1994**, 1773; d) C. M. Drain, J.-M. Lehn, *J. Chem. Soc. Chem. Commun.* **1994**, 2313; e) P. J. Stang, K. Chen, *J. Am. Chem. Soc.* **1995**, *117*, 1667; f) P. J. Stang, D. H. Cao, S. Saito, A. M. Arif, *J. Am. Chem. Soc.* **1995**, *117*, 6273; g) R. V. Slone, D. I. Yoon, R. M. Calhoun, J. T. Hupp, *J. Am. Chem. Soc.* **1995**, *117*, 11 813; h) M. Fujita, O. Sasaki, T. Mitsuhashi, T. Fujita, J. Yazaki, K. Yamaguchi, K. Ogura, *Chem. Commun.* **1996**, 1535; i) B. Olenyuk, J. A. Whiteford, P. J. Stang, *J. Am. Chem. Soc.* **1996**, *118*, 8221; j) P. J. Stang, N. E. Persky, *Chem. Commun.* **1997**, 77; k) H. Yan, G. Süss-Fink, A. Neels, H. Stoeckli-Evans, *J. Chem. Soc. Dalton Trans.* **1997**, 4345; l) J. Manna, C. J. Kuehl, J. A. Whiteford, P. J. Stang, D. C. Muddiman, S. A. Hofstadler, R. D. Smith, *J. Am. Chem. Soc.* **1997**, *119*, 11 611; m) S. B. Lee, S. Hwang, D. S. Chung, H. Yun, J.-I. Hong, *Tetrahedron Lett.* **1998**, *39*, 873; n) K. D. Benkstein, J. T. Hupp, C. L. Stern, *J. Am. Chem. Soc.* **1998**, *120*, 12 982; o) F. A. Cotton, L. M. Daniels, C. Lin, C. A. Murillo, *J. Am. Chem. Soc.* **1999**, *121*, 4538; p) F. Würthner, A. Sautter, *Chem. Commun.* **2000**, 445; q) F. Würthner, A. Sautter, D. Schmid, P. J. A. Weber, *Chem. Eur. J.* **2001**, *7*, 894.

[9] a) P. Chaudhuri, I. Karpenstein, M. Winter, C. Butzlaff, E. Bill, A. X. Trautwein, U. Flörke, H.-J. Haupt, *J. Chem. Soc. Chem. Commun.* **1992**, 321; b) D. P. Smith, E. Baralt, B. Morales, M. M. Olmstead, M. F. Maestre, R. H. Fish, *J. Am. Chem. Soc.* **1992**, *114*, 10 647; c) S. Rüttimann, G. Bernardinelli, A. F. Williams, *Angew. Chem.* **1993**, *105*, 432; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 392; d) H. Chen, M. M. Olmstead, D. P. Smith, M. F. Maestre, R. H. Fish, *Angew. Chem.* **1995**, *107*, 1590; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1514; e) R.-D. Schnebeck, L. Randaccio, E. Zangrando, B. Lippert, *Angew. Chem.* **1998**, *110*, 128; *Angew. Chem. Int. Ed.* **1998**, *37*, 119; f) R.-D. Schnebeck, E. Freisinger, B. Lippert, *Angew. Chem.* **1999**, *111*, 235; *Angew. Chem. Int. Ed.* **1999**, *38*, 168; g) S.-W. Lai, M. C.-W. Chan, S.-M. Peng, C.-M. Che, *Angew. Chem.* **1999**, *111*, 708; *Angew. Chem. Int. Ed.* **1999**, *38*, 669; h) R.-D. Schnebeck, E. Freisinger, B. Lippert, *Chem. Commun.* **1999**, 675; i) R.-D. Schnebeck, E. Freisinger, F. Glahé, B. Lippert, *J. Am. Chem. Soc.* **2000**, *122*, 1381; j) R. F. Carina, A. F. Williams, G. Bernardinelli, *Inorg. Chem.* **2001**, *40*, 1826.

Directing Topoisomerase I Mediated DNA Cleavage to Specific Sites by Camptothecin Tethered to Minor- and Major-Groove Ligands**

Paola B. Arimondo, Christian Bailly, Alexandre S. Boutorine, Vladimir A. Ryabinin, Alexandre N. Syniakov, Jian-Sheng Sun, Thérèse Garestier, and Claude Hélène*

Hairpin polyamides containing pyrrole– and imidazole–carboxamide units represent convenient tools to target specific sequences in DNA.[1] These compounds form dimeric motifs that fit snugly into the minor groove of B-DNA and recognize defined sequences through the formation of an array of hydrogen bonds and van der Waals contacts. They provide a paradigm for the design of small molecules that regulate genes.[2]

The sequence-recognition properties of hairpin polyamides can be exploited for directing DNA-cleaving and -alkylating agents to particular sequences.[3–7] By analogy, we reasoned that they could also be used to direct the action of DNA-cleaving proteins such as topoisomerases. These ubiquitous

[*] Prof. C. Hélène, Dr. P. B. Arimondo, Prof. A. S. Boutorine, Prof. J.-S. Sun, Prof. T. Garestier
Laboratoire de Biophysique, INSERM U201, UMR 8646 CNRS
Muséum National d'Histoire Naturelle
43 rue Cuvier, 75231 Paris cedex 05 (France)
Fax: (+33) 1-40793705
E-mail: helene@mnhn.fr

Dr. C. Bailly
INSERM U524 and Laboratoire de Pharmacologie Antitumorale
du Centre Oscar Lambret, IRCL
1 Place Verdun, 59045 Lille (France)

Dr. V. A. Ryabinin, Dr. A. N. Syniakov
Institute of Molecular Biology
State Research Center of Virology and Biotechnology "Vector"
Koltsovo, Novosibirsk region, 630559 (Russia)

[**] This work was supported by grants (to C.B.) from the Comité du Nord de la Ligue Nationale Française contre le Cancer. P.B.A. is the recipient of a postdoctoral fellowship from the Ligue Nationale Contre le Cancer.