

Unusual Luminescence of Hexapyrrolidine Derivatives of C₆₀ with T_h and Novel D₃-Symmetry

Georg Schick, Marcia Levitus, Lance Kvetko, Brent A. Johnson, Iris Lamparth, Ralph Lunkwitz, Bin Ma, Saeed I. Khan, Miguel A. Garcia-Garibay,* and Yves Rubin*

Department of Chemistry and Biochemistry
University of California, Los Angeles, California 90095-1569

Received December 15, 1998

The functionalization of fullerenes¹ offers new opportunities in the preparation of materials with building blocks having highly symmetrical and coordinating geometries. Hexaadducts with T_h-symmetry are particularly attractive targets, but they have been relatively difficult to access and are presently limited to mostly noncoordinating addends.² In an effort to explore the formation and potential of novel symmetrical hexaadducts of C₆₀, we have targeted the synthesis of fulleropyrrolidine hexanitroxide **2a**, a potential candidate for the construction of three-dimensional ferro- or ferrimagnets.^{3,4} This study reports the facile synthesis of its precursor **1a** and the discovery of a novel hexaadduct with D₃-symmetry (**1b**). Importantly, their modified fullerene π-systems display remarkable photophysical properties. A bright fluorescence that covers most of the visible range (λ_{max} = 540 nm) and a very intense, highly structured, and very long-lived phosphorescence (λ_{max} = 625 nm, t_{1/2} ≈ 4 s) have been investigated and characterized with a view that aims at the development of electroluminescent and magneto-optic media.

Regioselective formation of T_h-hexaadducts, mainly using the mild Bingel reaction, has been possible because the *e* (face) C=C bonds of products at every addition step show increasing selectivity toward further addition through LUMO control, an effect that can be enhanced by templating or solid-state conditions.² For the synthesis of hexaadduct **1a**, the large steric bias of the tetramethyl azomethine ylide **3** was found to be essential in adding to these effects.⁵ Indeed, reaction of C₆₀ with the ylide **3**, generated from a large excess of acetone and 2,2-dimethylglycine (DMG, 30 equiv), proceeded cleanly over 3–4 days to give a pale orange solution (PhCl, 160 °C). Initial formation of the monoadduct proceeded in 65% yield in accord with a similar report.^{4b} The formation of the higher adducts was very sensitive to the fact that PhCl and acetone have to be strictly dried over molecular sieves (4 Å). Upon monitoring of the reaction by TLC, unusually bright luminescent spots were observed for the tris- to hexaadducts.⁶ The tris- to pentaadducts fluoresce in shades of orange and red, and the hexaadducts **1a/b** have a strong yellow-

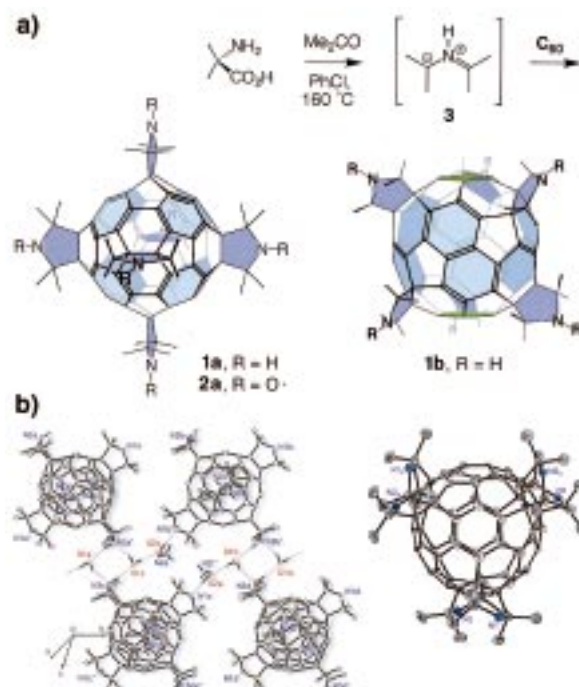


Figure 1. (a) Reaction scheme for hexapyrrolidine synthesis. (b) Left: Packing structure of hexaadduct **1a**. Right: X-ray structure of hexaadduct **1b** (ORTEP) viewed down the C₃-axis, with nitrogens in blue and sp³-carbons in gray.

green fluorescence. Intriguingly, multiple adducts in the *N*-methylpyrrolidine,⁵ Bingel,^{2b–c} or Diels–Alder^{2f} series appear not to show eye-detectable luminescence.

The isolation of the hexaadduct fraction from a minor pentaadduct fraction was performed by flash chromatography on silica gel with EtOAc/MeOH 6:1. Pure T_h-hexaadduct **1a** crystallized out of solution overnight into pale yellow prisms in 12% yield. Surprisingly, the unprecedented D₃-hexaadduct **1b** was found in the mother liquors upon evaporation. Compound **1b** is formed as an 80–90% component (¹H and ¹³C NMR) next to T_h-hexaadduct **1a** in combined yields as high as 73%, reflecting the extraordinary efficiency and selectivity of this reaction against a multitude of other possible products, despite the fact that no templating effect was used.^{2c} Difficult separation of the T_h- and D₃-hexaadducts **1a** and **1b** was achieved by flash chromatography on silica gel with toluene/MeOH/Et₃N 97:1.5:1.5 followed by concentration–crystallization from CS₂. These purifications had to be monitored by ¹H NMR since the two hexaadducts are not distinguishable by TLC or HPLC.

The high symmetry of T_h-hexaadduct **1a** is reflected by its very simple NMR features,⁶ showing only two signals in the proton spectrum and five lines in the ¹³C NMR spectrum. On the other hand, D₃-hexaadduct **1b** is distinguished by a clear reduction in symmetry manifested by four singlets with equal intensities (Me groups) in the ¹H NMR spectrum (CS₂/Me₂CO-*d*₆, 5:1). A total of eight peaks with equal intensities in the sp² region are observed in the ¹³C NMR spectrum, along with two sp³(C₆₀) peaks, two-quarternary carbons, and four methyl groups.

Both hexaadducts **1a** and **1b** were characterized by X-ray crystallography (Figure 1).⁶ The pseudo-octahedral structure of **1a** has its six symmetrically appended pyrrolidine rings puckered, reducing its averaged T_h-symmetry down to S₂. The molecules are tightly held by a three-dimensional hydrogen-bonded network comprising two crystallographically independent water molecules defined by O1x and O2x (x = a–d) connecting all secondary amine nitrogens, either in the *b,c*-plane (N1, N1', N3, N3') or

(1) (a) Hirsch, A. *The Chemistry of the Fullerenes*; Thieme: New York, 1994. (b) Diederich, F.; Thilgen, C. *Science* **1996**, *271*, 317–323.

(2) (a) Fagan, P. J.; Calabrese, J. C.; Malone, B. *J. Am. Chem. Soc.* **1991**, *113*, 9408–9409. (b) A. Hirsch, I. Lamparth, T. Grösser, H. R. Karfunkel, *J. Am. Chem. Soc.* **1994**, *116*, 9385–9386. (c) Lamparth, I.; Herzog, A.; Hirsch, A. *Tetrahedron* **1996**, *52*, 5065–5075. (d) Isaacs, L.; Diederich, F.; Haldimann, R. F. *Helv. Chim. Acta* **1997**, *80*, 317–342. (e) Schwenninger, R.; Müller, T.; Kräutler, B. *J. Am. Chem. Soc.* **1997**, *119*, 9317–9318. (f) Kräutler, B.; Maynollo, J. *Tetrahedron* **1996**, *52*, 5033–5042.

(3) (a) Caneschi, A.; Gatteschi, D.; Sessoli, R.; Paul, R. *Acc. Chem. Res.* **1989**, *22*, 392–398. (b) Chiarelli, R.; Rassat, A.; Rey, P. *J. Chem. Soc., Chem. Commun.* **1992**, 1081–1082. (c) Stumpf, H. O.; Ouahab, L.; Pei, Y.; Grandjean, D.; Kahn, O. *Science* **1993**, *261*, 447–449. (d) Inoue, K.; Hayamizu, T.; Iwamura, H.; Hashizume, D.; Ohashi, Y. *J. Am. Chem. Soc.* **1996**, *118*, 1803–1804.

(4) (a) Arena, F.; Bullo, F.; Conti, F.; Corvaja, C.; Maggini, M.; Prato, M.; Scorrano, G. *J. Am. Chem. Soc.* **1997**, *119*, 789–795. (b) Li, Y. L.; Mao, Z.; Xu, J. H.; Yang, Y. K.; Guo, Z. X.; Zhu, D. B.; Li, J. W.; Yin, B. *Chem. Phys. Lett.* **1997**, *265*, 361–364. (c) Ishida, T.; Shinozuka, K.; Nogami, T.; Kubota, M.; Ohashi, M. *Tetrahedron* **1996**, *52*, 5103–5112.

(5) Other azomethine ylide additions have been characterized by low regioselectivity: Pasimeni, L.; Hirsch, A.; Lamparth, I.; Herzog, A.; Maggini, M.; Prato, M.; Corvaja, C.; Scorrano, G. *J. Am. Chem. Soc.* **1997**, *119*, 12896–12901 and references therein.

(6) See Supporting Information.

above and below that plane along the a -axis ($N2$, $N2'$).⁷ Heteroatom to hydrogen distances correspond to distances of normal H-bonds.⁶ The molecules are tightly packed as shown by center-to-center distances between hexaadduct units of 14.108 Å along the b -axis and 15.365 Å along the median of the b,c -axes, while the largest intramolecular N–N distances, for pyrrolidines with *trans*-1 relationship, average 12.085 Å. The N–N distance in 4,4'-dicyanobiphenyl is 12.16 Å for size comparison.⁸

The helical chirality of the D_3 -symmetric structure **1b** is illustrated in the view down the C_3 -axis of Figure 1. This remarkable symmetry has no precedence in fullerene chemistry. The fact that the D_3 -hexaadduct **1b** is formed preferentially to the T_h -hexaadduct **1a** must originate from the primary distribution of bisadduct regioisomers,^{5,6} with steric hindrance strongly influencing all subsequent additions. The D_3 -hexaadduct **1b** has its six addends either in *cis*-3, *e*, *trans*-3, or *trans*-2 relationships, whereas the T_h -hexaadduct **1a** has only *e* or *trans*-1 relationships.^{2b} We have observed that the *trans*-3 bisadduct is formed preferentially and must influence the outcome of all subsequent additions up to the hexaadduct **1b** in conjunction with the other formed regioisomers.⁶ This precept will be verified in future work.

The strong luminescence observed by TLC and in solution for the T_h - and D_3 -hexaadducts **1a** and **1b** and their lower addition precursors indicates photophysical properties that are unusual in comparison with other fullerene derivatives.⁹ The photophysics of C_{60} and its monofunctionalized adducts are characterized by exceedingly slow radiative transitions and very fast intersystem crossing to the triplet. Accordingly, the fluorescence quantum yields of C_{60} ($\Phi_f = 3.2 \times 10^{-4}$ in toluene), several monopyrrolidines ($\Phi_f = 10.0\text{--}11.8 \times 10^{-4}$, C_6H_6), and other monoadducts ($\Phi_f = \sim 10^{-4}$) are all very weak and in the near-infrared ($\lambda_{\max} 700\text{--}1000$ nm).¹⁰ In the case of C_{60} , triplet lifetimes of 40 μ s in argon-saturated benzene solution at ambient temperature¹¹ barely extend by a factor of 10, to 410 μ s, upon cooling to 1.2 K in hydrocarbon glasses.¹² Since the phosphorescence emission of C_{60} is overwhelmed by its weak fluorescence, despite triplet yields that are near unity, one must conclude that slow triplet-state radiative rates do not compete with the very fast thermal decays by intersystem crossing to the ground singlet state.

In contrast to the above photophysical data, dilute solutions of T_h - and D_3 -hexaadducts **1a** and **1b** at 25 °C in methylcyclohexane (MCH) showed a remarkable shift to the visible with $\lambda_{\max} = 550$ nm, and a ca. 20-fold increase in quantum yields (0.024 and 0.020, respectively) as compared to other adducts. Fluorescence decays were single exponential with values of 3.7 ± 0.2 and 3.1 ± 0.2 ns at 25 °C for **1a** and **1b**, respectively. Upon cooling these solutions to 77 K, two bright orange, well-resolved, and intense phosphorescence emissions, with lifetimes of 4.4 and 3.7 s, appeared between 615 and 800 nm (Figure 2).

The photophysical properties of hexaadducts **1a** and **1b** in comparison to those of C_{60} can be understood primarily in terms of their diminished π -system. The radiative fluorescence rate of hexaadducts **1a** and **1b**, obtained from their fluorescence yields and lifetimes, is about 10^3 times as fast as that of C_{60} . Remarkably,

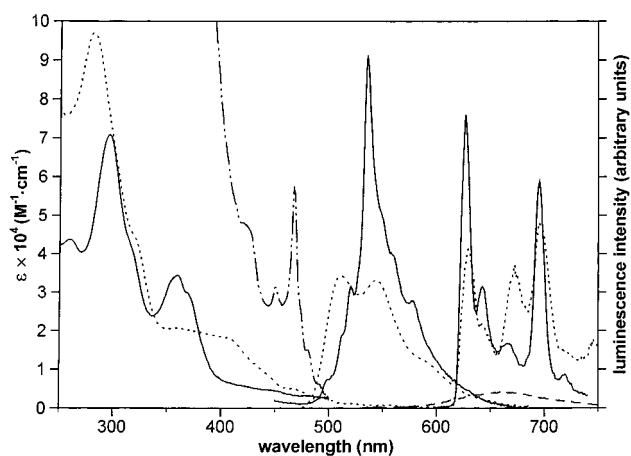


Figure 2. Electronic absorption (CH_2Cl_2 , 25 °C), fluorescence (25 °C), and phosphorescence spectra (77 K) of the T_h (—) and D_3 (····) hexaadducts **1a** and **1b**. Excitation spectrum of **1a** (- · - ·) at 77 K ($\lambda_{\text{em}} = 540$ nm) and fluorescence spectrum of **4** (- - -).

intersystem crossing from the singlet to the triplet state still enjoys a very efficient spin-orbit coupling and accounts for ca. 97% of the singlet decay. The phosphorescence intensity of **1a** and **1b** is very high, primarily because the thermal decay of their triplet state, estimated from their phosphorescence lifetimes, is at least 10^6 times slower than that of C_{60} . These changes are consistent with the following spectral properties observed: While a greater singlet energy, given by a ~ 150 -nm blue shift relative to C_{60} , increases the transition dipole moment and the radiative rate from the singlet state, a larger triplet-to-ground-state energy gap decreases the rate of all radiation-less transitions from the triplet. To test this interpretation, we analyzed a structurally related Bingel-type T_h - (dicarboethoxycyclopropyl)hexaadduct (**4**)^{2b,c} with a higher degree of delocalization by homoconjugation. As expected, with an absorbance that is ca. 100 nm red-shifted with respect to those of the hexapyrrolidines, hexaadduct **4** has a red fluorescence with a λ_{\max} at 673 nm and a lower quantum yield of 30×10^{-4} . We made no attempts at measuring its near-infrared phosphorescence. To test whether amine nitrogen to fullerene charge transfer plays a role on the photophysics of **1a** and **1b**, we carried out solvent-polarity and protonation studies with CF_3COOH . The answer is negative: A very small change in dipole moment upon electronic excitation for **1a** and **1b** was deduced from the very small changes in absorbance and emission observed in methylcyclohexane, CH_2Cl_2 , MeCN, and EtOH. Protonation of **1b** (D_3 -hexaadduct) with 1% $\text{CF}_3\text{CO}_2\text{H}$ in ethanol caused no changes in emission intensities or lifetimes. Protonation of T_h -hexaadduct **1a** showed a small Stokes shift of ca. 25 nm along with a 2-fold increase in fluorescence quantum yields ($\Phi = 0.043$) and a small decrease in phosphorescence intensities. Minor changes as a function of polarity and protonation suggest that charge transfer plays a relatively minor role in the photophysics of the singlet excited state.

The prime emission positions of the hexaadducts **1a** and **1b** and their relatively high quantum yields suggest their applicability in electroluminescent devices and light-harvesting dendrimeric systems. High steady-state concentrations (up to 45%) of the very intense triplet-state emissions also suggest their possible use in magneto-optic applications.

Acknowledgment. We are grateful to the Beckman Foundation for a BYI Award (Y.R.) and the NSF for a NYI award (CHE-9457693, Y.R.) and grant (CHE-9624950, M.A.G.G.). We thank Dr. Charles F. Campana of Bruker Analytical X-ray Systems for data collection and refinement of **1b**.

Supporting Information Available: Experimental procedures, characterization data, stereoscopic views, and X-ray tables for **1a** and **1b**; additional details for lower addition products (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA984329K

(7) For a C–H···O bonded network of a C_{60} -hexaadduct, see: Seiler, P.; Isaacs, L.; Diederich, F. *Helv. Chim. Acta* **1996**, *79*, 1047–1058.

(8) Hirsch, K. A.; Venkataraman, D.; Wilson, S. R.; Moore, J. S.; Lee, S. *J. Chem. Soc., Chem. Commun.* **1995**, 2199–2200.

(9) Avent, A. G.; Birkett, P. R.; Darwish, A. D.; Kroto, H. W.; Taylor, R. *Tetrahedron* **1996**, *52*, 5235–5246.

(10) (a) Sun, Y.-P.; Lawson, G. E.; Riggs, J. E.; Ma, B.; Wang, N.; Moton, D. K. *J. Phys. Chem. A* **1998**, *102*, 5520–5528. (b) Luo, C.; Fujitsuka, M.; Watanabe, A.; Ito, O.; Gan, L.; Huang, Y.; Huang, C. H. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 527–532. (c) Williams, R. M.; Zwier, J. M.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 4093–4099. (d) Lin, S. K.; Shiu, L. L.; Chien, K. M.; Luh, T. Y.; Lin, T. I. *J. Phys. Chem.* **1995**, *99*, 105–111. (e) Matsuura, Y.; Muraoka, H.; Tada, H.; Yoshida, Z. *Chem. Lett.* **1996**, 373–374.

(11) Arbogast, J. W.; Darmanyan, A. P.; Foote, C. S.; Rubin, Y.; Diederich, F. N.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Phys. Chem.* **1991**, *95*, 11–12.

(12) (a) van den Heuvel, D. J.; Chan, I. Y.; Groenen, E. J. J.; Schmidt, J.; Meijer, G. *Chem. Phys. Lett.* **1994**, *231*, 111–118. (b) Zeng, Y.; Biczok, L.; Linschitz, H. *J. Phys. Chem.* **1992**, *96*, 5237–5239.