Fullerene/Azacalixarene Complexes

Synthesis, Structure, and [60]Fullerene Complexation Properties of Azacalix[*m*]arene[*n*]pyridines**

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Since Atwood et al.[1] and Shinkai et al.[2] independently discovered the selective formation of a sparingly soluble C_{60}/*p*-*t*Bu-calix[8]arene complex in toluene in 1994, there has been an increasing interest in supramolecular fullerene chemistry because of its potential applications in chemistry, biology, and materials sciences.[3] The design of host molecules capable of recognizing fullerenes, one of the most challenging and thrilling tasks in this field, is mainly based on the complementarity principle. The utilization of concave/convex interaction, for example, has resulted in the emergence of a few macrocyclic [60]fullerene receptors such as calix[*n*]arenes,[1,2,4] homooxacalix[3]arene,[4b,5] γ-cyclodextrin (γ-CD),[6] cyclotriveratrylene (CTV),[7] and crown ethers.[8] Intriguingly, however, porphyrins and metalloporphyrins with planar π surfaces have also been shown to interact with the curved π surface of fullerenes, predominantly through van der Waals dispersion forces.[9] To enhance the complexation power of receptors or to increase the stability of complexes, strategies for constructing molecular clefts such as bis(calix[*n*]arenes)[10] and "jaws porphyrins"[11] have been successfully followed.

The past decade has seen a tremendous development in calixarene chemistry, and it has now become an indispensable part of supramolecular chemistry.[12–15] While efforts are still being expended on derivatization of basic calixarene skeletons to improve their cavities and therefore their selective recognition properties towards various guest molecules, a

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more recent development in this field is the construction of new calixarenes by replacing the methylene bridges with heteroatoms[16] such as nitrogen,[17] sulphur,[18] and other elements,[16,19] or their phenol units with pyrrole,[20] pyridine,[21] and other heteroarene species.[16,22] This has led to a number of intriguing macrocycles, such as thiacalixarenes[18] and calixpyrroles.[20] To develop novel and efficient host molecules, we envisaged that the incorporation of nitrogen atoms into calixarenes would generate intriguing azacalixarenes and azacalixpyridines or their hydrides. Because the bridging amino-nitrogen atoms can adopt sp^3- and/or sp^2-hybridized configurations with or without conjugation to the neighboring benzene or pyridine rings, the designed macrocycles would be subject to self-tuning by formation of various cavities corresponding to the presence or absence of a guest species. The conjugative effect of the bridging amino groups would also increase the electron density of the π surface of the resulting concave molecules and therefore enhance the binding affinity towards the electron-deficient curved π surfaces of fullerenes. Here we report a convenient fragment-coupling synthesis of novel azacalix[*m*]arene[*n*]pyridine host molecules, their molecular structures, and unique fullerene-complexation properties.

As illustrated in Scheme 1, *m*-phenylenediamine (**1**) condensed efficiently with 2,6-dibromopyridine (**2**) in the presence of an excess of KO*t*Bu to afford *N*,*N*′-bis(6′-bromopyrid-2′-yl)-*m*-phenylenediamine (**3**) in excellent yield. Treatment of **3** with methyl iodide and KO*t*Bu led efficiently to the formation of molecular fragment **4** in 90% yield. Palladium-catalyzed double aryl amination[23] of **4** with *N*,*N*′-dimethyl-*m*-phenylenediamine (**5**) in refluxing toluene furnished macrocyclic azacalix[2]arene[2]pyridine **6** ($n=1$) and azacalix[4]arene[4]pyridine **7** ($n=3$) in 26 and 22% yields, respectively (see Supporting Information). When the intermolecular cyclocondensation of **4** and **5** was performed at lower temperature (104 °C), the larger ring compound **7** was obtained as the major product in 26% yield.

Recrystallization of **6** from hexane/ethyl acetate gave crystals suitable for X-ray structure analysis.[27] As shown in Figure 1, **6** adopts a heavily twisted 1,3-alternate conformation. This is in sharp contrast to the solid-state structures of

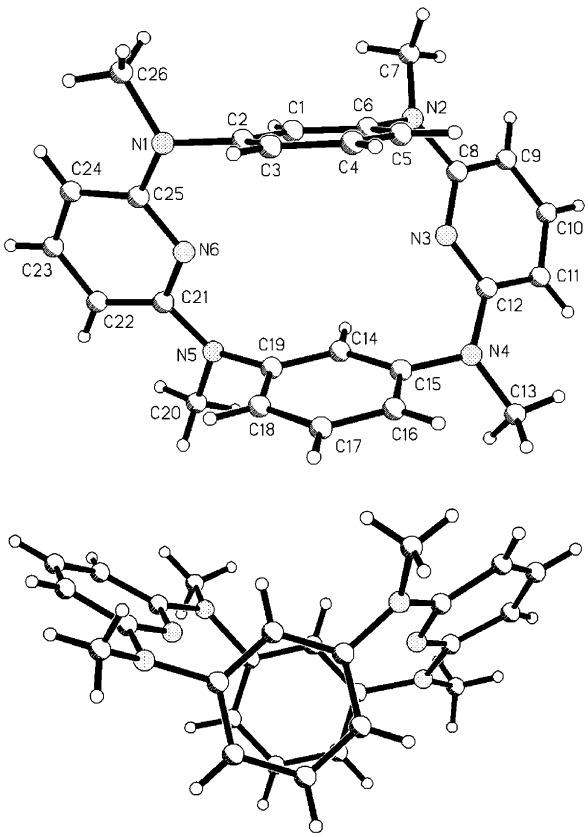
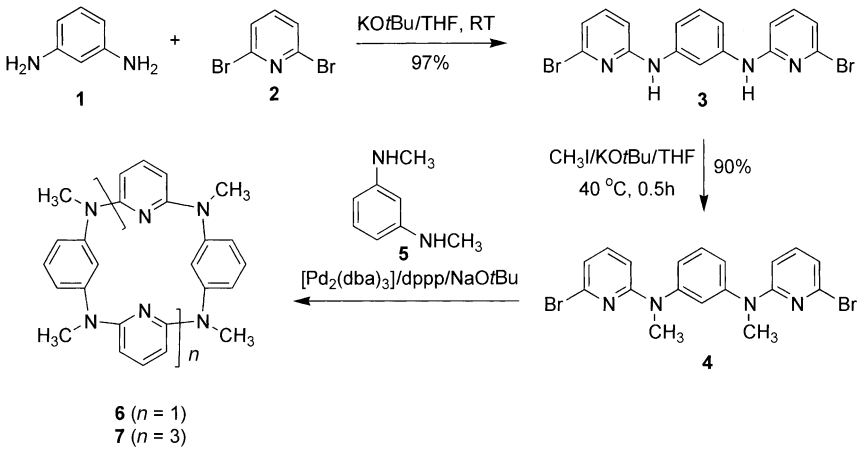


Figure 1. X-ray crystal structure of **6**.

azacalix[4]arene[17a] and of calix[4]pyridine,[21a] which have been determined as S_4 and a partial-cone conformation, respectively. Two of the benzene rings in the structure are almost face-to-face parallel but with a twist angel of 30°. The shortest C–C distance between these rings is 4.36 Å (C1–C14), while the C4–C17 distance is 5.09 Å. Interestingly, the crystal structure also reveals that all bridging amino groups conjugate with the neighboring pyridine rings rather than with benzene rings, with the two pairs of methyl groups located on the two pyridine planes. The four methyl groups are approximately *cis*-configured (rccc). The cavity of the azacalix[2]arene[2]pyridine **6** can be regarded as being constructed by two benzene and two conjugated 2,6-bis(methylamino)pyridine planar segments in a twisted 1,3-*alternate* fashion (Figure 1).

X-ray structure analysis of single crystals of azacalix[4]arene[4]pyridine **7**,[27] which were obtained directly from petroleum ether/ethyl acetate after column chromatography, showed an interesting molecular structure. First, as in **6**, all the bridging amino groups in **7** conjugate with the pyridine rings rather than with the benzene rings, and all methyl groups lie on the planes of the neighboring pyridine rings. Thus, all



Scheme 1. Fragment-coupling approach to azacalix[4]pyridine.

nitrogen atoms of the bridging amino groups adopt sp^2 configurations, and the macrocycle is derived from four benzene rings and four conjugated 2,6-bis(methylamino)pyridine planar units. Second, the molecule forms a large, diamond-shaped cavity in which the longest distance between two opposite benzene rings is 12.2 Å (Figure 2, top view). In

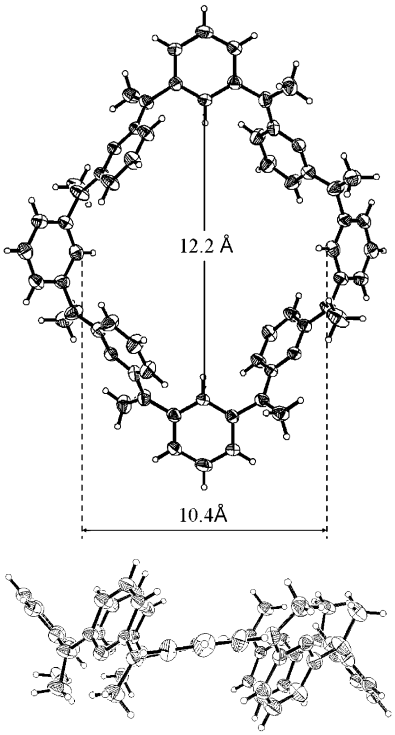


Figure 2. X-ray crystal structure of **7**.

addition, the whole cavity of the molecule is composed of two identical partial cone loops consisting of one benzene and two 2,6-bis(methylamino)pyridine planar segments. These two loops of opposite orientation are connected by two benzene moieties such that the molecule has S_2 symmetry. Accordingly, there are two sets of four *cis*-configured methyl groups (rccctttt) attached to the bottom rims of the two partial cone loops. The conformation of the molecule can thus be viewed as a 1,2,3-*partial cone*, resembling a double-ended spoon (Figure 2, side view). Furthermore, four pyridine nitrogen atoms lie on one plane, while eight bridging nitrogen atoms form another two rectangular planes.

Azacalix[*m*]arene[*n*]pyridines exhibit interesting [60]fullerene-complexation properties that depend on the size of the macrocyclic ring. By means of spectrophotometric measurements, for example, we found that **7** can strongly complex [60]fullerene, whereas its smaller homologue **6** has no affinity towards [60]fullerene. On addition of **7** to a solution of [60]fullerene in toluene, the absorption at 437.5 nm in the UV/Vis spectrum increases in intensity and shifts gradually to 452.5 nm (Supporting Information, Figure S1). The interaction of **7** with [60]fullerene was clearly evidenced by a color change of [60]fullerene in toluene from characteristic red-purple to light brown (Figure 3). A Job plot[10c,24] indicated 1:1

Figure 3. Color change from red-purple (left, $[C_{60}] = 1.084 \times 10^{-4}$ mol dm^{-3}) to light brown (right) on complexation with **6** (middle, colorless, 1.084×10^{-4} mol dm^{-3}).

complexation of **7** with [60]fullerene in toluene (Supporting Information, Figure S2). To further study the recognition of [60]fullerene by **7**, a fluorescence titration was conducted (Figure 4). The fluorescence intensity of **7** at about $\lambda_{em} =$ 402 nm decreased constantly with increasing concentration

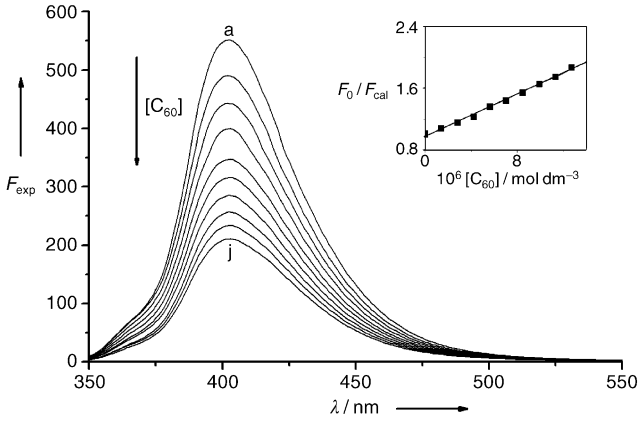


Figure 4. Emission spectra ($\lambda_{exc} = 336$ nm) of **7** (3.423×10^{-6} mol dm^{-3}) in the presence of C_{60} in toluene at 25 °C. The concentrations of C_{60} for curves a–j (from top to bottom) are 0.0, 1.419, 2.837, 4.256, 5.675, 7.093, 8.512, 9.931, 11.349, and 12.768×10^{-6} mol dm^{-3}. Inset: Variation of fluorescence intensity F_0/F_{cal} of **7** with increasing C_{60} concentration.

of [60]fullerene. To eliminate the competitive absorption of [60]fullerene at both the excitation and emission wavelengths, the fluorescence intensity F_{exp} of **7** was calibrated to F_{cal} according to a literature method.[25] The quenching was found to follow a Stern–Volmer equation, and the dependence of calibrated F_0/F_{cal} on the concentration of [60]fullerene is illustrated in the inset to Figure 4. The stability constant K_s calculated from the plot of F_0/F_{cal} versus [60]fullerene concentration is $70\,680 \pm 2060\ \text{M}^{-1}$.[26] To the best of our knowledge, this is the largest K_s value obtained up to date for complexation of [60]fullerene with a mono-macrocyclic receptor other than molecular clefts such as biscalix[*n*]arenes[10] and "jaws porphyrins".[11]

Azacalix[4]arene[4]pyridine **7** has even higher complexation capability towards [70]fullerene. As indicated by the

UV/Vis spectrum (Supporting Information, Figure S3) and the Job plot[10c,24] (Supporting Information, Figure S4), **7** also forms a 1:1 complex with [70]fullerene. A fluorescence titration revealed a stability constant K_s of $136620 \pm 3770\,M^{-1}$, almost twice the stability constant for complexation of **7** and [60]fullerene (see Supporting Information, Figure S5). The stronger affinity of **7** towards [70]fullerene than towards [60]fullerene is most probably due to the giant cavity and the oval shape.[28]

We hoped to determine the solid-state structures of the **7**-[60]fullerene and **7**-[70]fullerene complexes, but no crystals could be obtained. No salient changes were observed in the ^1H and ^{13}C NMR spectra of the complexes in solution. The superior complexation of fullerenes by **7**, which contrasts with the noninteraction between **6** and fullerenes, suggests a steric requirement for fullerene recognition by the macrocyclic receptor. This is consistent with the results of [60]fullerene recognition with different calix[*n*]arenes.[4b] The much higher affinity of **7** ($K_s = 70680 \pm 2060\,M^{-1}$) relative to calix[5]- and [6]arene derivatives ($K_s = 87$–$2120\,M^{-1}$)[4b,d,e] and homooxacalix[3]arene ($K_s = 35 \pm 5\,M^{-1}$)[4b] indicates a clear advantage of introducing amino groups into the bridging positions of calixarenes. However, the strong interaction of **7** with fullerenes is not due to the formation of charge-transfer complexes, because neither new absorption nor emission peaks were observed in spectrophotometric titrations. The precise reason for efficient complexation of fullerenes by azacalix[4]arene[4]pyridine still remains unclear, although it is most probably rationalizble as the van der Waals force between sterically fitted concave and convex π surfaces. The introduction of electron-donating amino groups as the bridging units increases the electron density of the aromatic rings, and therefore might further contribute to enhancing the interaction of the curved surface of the macrocyclic receptor with electron-deficient fullerenes.

In summary, we have developed a fragment-coupling approach for the synthesis of azacalix[*m*]arene[*n*]pyridines. In the solid state, azacalix[2]arene[2]pyridine **6** and azacalix[4]-arene[4]pyridine **7** adopt a heavily twisted 1,3-*alternate* conformation and a double-ended spoon-shaped 1,2,3-*partial cone* conformation, respectively, in which the bridging nitrogen atoms conjugate with the neighboring pyridine rings. We have also shown that **7** is a novel and efficient macrocyclic host molecule that complexes [60]- and [70]fullerene in toluene with K_s values of $70680 \pm 2060\,M^{-1}$ and $136620 \pm 3770\,M^{-1}$, respectively. The color change of [60]fullerene on complexation and the linearity of the plot of F_0/F_{cal} of the receptor against [60]fullerene concentration make **7** a powerful spectrophotometric sensor for [60]fullerene.

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[1] J. L. Atwood, G. A. Koutsantonis, C. L. Raston, *Nature* **1994**, *368*, 229.
[2] T. Suzuki, K. Nakashima, S. Shinkai, *Chem. Lett.* **1994**, 699.
[3] For reviews, see:a) F. Diederich, M. Gomez-Lopez, *Chem. Soc. Rev.* **1999**, *28*, 263; b) Z.-L. Zhong, A. Ikeda, S. Shinkai, Complexation of Fullerenes in *Calixarenes 2001* (Eds.: Z. Asfari, V. Bohmer, J. Vicens, M. Saadioui), Kluwer Academic Publishers, The Netherlands, **2001**, pp. 476–495.
[4] a) R. M. Williams, J. W. Verhoeven, *Recl. Trav. Chim. Pays-Bas* **1992**, *111*, 531; b) A. Ikeda, Y. Suzuki, M. Yoshimura, S. Shinkai, *Tetrahedron* **1998**, *54*, 2497; c) M. Makha, M. J. Hardie, C. L. Raston, *Chem. Commun.* **2002**, 1446; d) H. Haino, M. Yanase, Y. Fukazawa, *Angew. Chem.* **1997**, *109*, 288; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 259; e) T. Haino, M. Yanase, Y. Fukazawa, *Angew. Chem.* **1998**, *110*, 1044; *Angew. Chem. Int. Ed.* **1998**, *37*, 997; f) J. L. Atwood, L. J. Barbour, C. L. Raston, I. B. N. Sudria, *Angew. Chem.* **1998**, *110*, 1029; *Angew. Chem. Int. Ed.* **1998**, *37*, 981.
[5] a) K. Tsubaki, K. Tanaka, T. Kinoshita, K. Fuji, *Chem. Commun.* **1998**, 895; b) A. Ikeda, T. Hatano, S. Shinkai, T. Akiyama, S. Yamada, *J. Am. Chem. Soc.* **2001**, *123*, 4855.
[6] Z.-I. Yoshida, H. Yakekuma, S.-I. Takekuma, Y. Matsubara, *Angew. Chem.* **1994**, *106*, 1658; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1597.
[7] J. L. Atwwod, M. J. Barnes, M. G. Gardiner, C. L. Raston, *Chem. Commun.* **1996**, 1449.
[8] S. Bhattacharya, A. Sharma, S. K. Nayak, S. Chattopadhyay, A. K. Mukherjee, *J. Phys. Chem. B* **2003**, *107*, 4213.
[9] a) Y. Sun, T. Drovetskaya, R. D. Bolskar, R. Bau, P. D. W. Boyd, C. A. Reed, *J. Org. Chem.* **1997**, *62*, 3642; M. M. Olmstead, D. A. Costa, K. Maitra, B. C. Noll, S. L. Phillips, P. M. Van Calcar, A. L. Balch, *J. Am. Chem. Soc.* **1999**, *121*, 7090; c) P. D. W. Boyd, M. C. Hodgson, C. E. F. Rickard, A. G. Oliver, L. Chaker, P. J. Brothers, R. D. Bolskar, F. S. Tham, C. A. Reed, *J. Am. Chem. Soc.* **1999**, *121*, 10487.
[10] a) T. Haino, M. Yanase, Y. Fukazawa, *Angew. Chem.* **1998**, *110*, 1044; *Angew. Chem. Int. Ed.* **1998**, *37*, 997; b) L. Wang, C. D. Gutsche, *J. Am. Chem. Soc.* **1998**, *120*, 12226; c) J. Wang, S. G. Bodige, W. H. Watson, C. D. Gutsche, *J. Org. Chem.* **2000**, *65*, 8260; d) T. Haino, H. Araki, Y. Fujiwara, Y. Tanimoto, Y. Fukazawa, *Chem. Commun.* **2002**, 2148; T. Haino, Y. Yamanaka, H. Araki, Y. Fukazawa, *Chem. Commun.* **2002**, 402.
[11] a) D. Sun, F. S. Tham, C. A. Reed, L. Chaker, M. Burgess, P. D. W. Boyd, *J. Am. Chem. Soc.* **2000**, *122*, 10704b) J.-Y. Zheng, K. Tashiro, Y. Hirabayashi, K. Kinbara, K. Saigo, T. Aida, S. Sakamoto, K. Yamaguchi, *Angew. Chem.* **2001**, *113*, 1909; *Angew. Chem. Int. Ed.* **2001**, *40*, 1857; c) Y. Kubo, A. Sugasaki, M. Ikeda, K. Sugiyasu, K. Sonoda, A. Ikeda, M. Takeuchi, S. Shinkai, *Org. Lett.* **2002**, *4*, 925; d) M. Ayabe, A. Ikeda, S. Shinkai, S. Sakamoto, K. Yamaguchi, *Chem. Commun.* **2002**, 1032; e) M. Ayabe, A. Ikeda, Y. Kubo, M. takeuchi, S. Shinkai, *Angew. Chem.* **2002**, *114*, 2914; *Angew. Chem. Int. Ed.* **2002**, *41*, 2790; f) D. Sun, F. S. Tham, C. A. Reed, L. Chaker, P. D. W. Boyd, *J. Am. Chem. Soc.* **2002**, *124*, 6604.
[12] *Calixarenes 2001* (Eds.: Z. Asfari, V. Böhmer, J. Harrowfield, J. Vicens, M. Saadioui), Kluwer Academic Publishers, Dordrecht, **2001**.
[13] C. D. Gutsche, *Calixarenes Revisited*, The Royal Society of Chemistry, Cambridge, **1998**.
[14] *Calixarenes in Action* (Eds.: L. Mandolini, R. Ungaro), Imperial College, London, **2000**.
[15] G. J. Lumetta, R. D. Rogers, A. S. Gopalan, *Calixarenes for Separation*, ACS, Washington, **2000**.
[16] For a useful overview of heteroatom-bridged calixarenes, see B. König, M. H. Fonseca, *Eur. J. Inorg. Chem.* **2000**, 2303.
[17] a) A. Ito, Y. Ono, K. Tanaka, *New J. Chem.* **1998**, 779; b) A. Ito, Y. Ono, K. Tanaka, *J. Org. Chem.* **1999**, *64*, 8236.
[18] a) H. Kumagai, M. Hasegawa, S. Miyanari, Y. Sugawa, Y. Sato, T. Hori, S. Ueda, H. Kamiyama, S. Miyano, *Tetrahedron Lett.* **1997**,

38, 3971; b) H. Iki, C. Kabuto, T. Fukushima, H. Kumagai, H. Takeya, S. Miyanari, T. Miyashi, S. Miyano, *Tetrahedron* **2000**, *56*, 1437; c) H. Akdas, L. Bringel, E. Graf, M. W. Hosseini, G. Mislin, J. Pansanel, A. De Cian, J. Fischer, *Tetrahedron Lett.* **1998**, *39*, 2311.

[19] a) E. E. Boros, C. W. Andrews, A. O. Davis, *J. Org. Chem.* **1996**, *61*, 2553; b) B. König, M. Rödel, P. Bubenitschek, P. G. Jones, I. Thondorf, *J. Org. Chem.* **1995**, *60*, 7406; c) M. Yoshida, M. Goto, F. Nakanishi, *Organometallics* **1999**, *18*, 1465.

[20] a) P. A. Gale, J. L. Sessler, V. Král, *Chem. Commun.* **1998**, 1; b) S. Depraetere, M. Smet, W. Dehaen, *Angew. Chem.* **1999**, *111*, 3556; *Angew. Chem. Int. Ed.* **1999**, *38*, 3359; c) B. Turner, A. Shterenberg, M. Kapon, K. Suwinska, Y. Eichen, *Chem. Commun.* **2001**, 13; d) C. Bucher, R. S. Zimmerman, V. Lynch, V. Král, J. L. Sessler, *J. Am. Chem. Soc.* **2001**, *123*, 2099; e) G. Cafeo, F. H. Kohnke, G. L. La Torre, M. F. Parisi, R. P. Nascone, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **2002**, *8*, 3148; f) C. Floriani, *Chem. Commun.* **1996**, 1257; g) P. A. Gale, P. Anzenbacher, J. L. Sessler, *Coord. Chem. Rev.* **2001**, *222*, 57.

[21] a) V. Král, P. A. Gale, P. Anzenbacher, K. Jursiková, V. Lynch, J. L. Sessler, *Chem. Commun.* **1998**, 9; b) J. L. Sessler, W.-S. Cho, V. Lynch, V. Král, *Chem. Eur. J.* **2002**, *8*, 1134; c) T. Gerkensmeier, J. Mattay, C. Näther, *Chem. Eur. J.* **2001**, *7*, 465.

[22] a) P. R. Dave, G. Doyle, *J. Org. Chem.* **1995**, *60*, 6946; b) N. Avarvari, N. Mezailles, L. Richard, P. Le Floch, F. Mathey, *Science* **1998**, *280*, 1587c) E. Vogel, M. Pohl, A. Herrmann, T. Wiss, C. König, J. Lex, M. Gross, J. P. Gisselbrecht, *Angew. Chem.* **1996**, *108*, 1677; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1520; d) J. Guillard, O. Meth-Cohn, C. W. Rees, A. J. P. White, D. J. Williams, *Chem. Commun.* **2002**, 232.

[23] S. Wagaw, S. L. Buchwald, *J. Org. Chem.* **1996**, *61*, 7240.

[24] J. Polster, H. Lachmann, *Spectrometric Titrations*, VCH, **1989**, pp. 256–259.

[25] M. Zheng, F. Bai, F. Li, D. Zhu, *J. Appl. Polym. Sci.* **1998**, *70*, 599.

[26] J. Wang, D. Wang, E. K. Miller, D. Moses, G. C. bazan, A. J. Heeger, *Macromolecules* **2000**, *33*, 5153. Both static and dynamic quenching processes can be quantitatively described by the Stern–Volmer equation: $F_0/F = 1 + K_{sv}[\text{quencher}]$, where the F_0 is the fluorescence intensity in the absence of the quencher, and F the fluorescence intensity in the presence of the quencher. The Stern–Volmer constant K_{sv} provides a quantitative measure of the quenching. In static quenching, the Stern–Volmer constant is the association constant for complex formation, that is, $K_{sv}^{S} = [FQ]/[F][Q]$, where [FQ], [F], and [Q] are the concentrations of complex, fluorophore, and quencher, respectively. From the above equation, it is straightforward to calculate the probability f that a fluorophore is not complexed: $f = [F]/([F] + [FQ]) = 1/(1 + K_{sv}^{S}[Q]) = F/F_0$ In our case, the stability constant K_s was calculated from the equation $F_0/F_{cal} = 1 + K_s[\text{fullerene}]$.

[27] Crystal data for **6** ($C_{26}H_{26}N_6$): $M_r = 422.53$, triclinic, space group $P\bar{1}$, $a = 9.6577(10)$, $b = 9.9349(11)$, $c = 12.3553(7)$ Å, $\alpha = 90.132(5)$, $\beta = 104.705(4)$, $\gamma = 109.768(3)°$, $V = 1074.0(17)$ Å^3, $T = 293(2)$ K, $Z = 2$, $\rho_{calcd} = 1.307$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.081$ mm^{-1}; of a total of 7449 reflections, 4752 unique reflections ($R_{int} = 0.0523$) were used in the refinement by full-matrix least-squares methods on F^2, which converged to $R_F = 0.0649$ [$I > 2\sigma(I)$], 0.0935 (all data) and $Rw(F^2) = 0.1853$ [$I > 2\sigma(I)$], 0.2007 (all data). Crystal data for **7**·2 H_2O ($C_{52}H_{56}N_{12}O_2$): $M_r = 881.09$, triclinic, space group $P\bar{1}$, $a = 8.8164(18)$, $b = 11.5548(18)$, $c = 13.538(2)$ Å, $\alpha = 78.438(12)$, $\beta = 89.066(6)$, $\gamma = 75.572(3)°$, $V = 1307.8(4)$ Å^3, $T = 293(2)$ K, $Z = 1$, $\rho_{calcd} = 1.119$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.071$ mm^{-1}; of a total of 9311 reflections, 5837 unique reflections ($R_{int} = 0.0471$) were used in the refinement by full-matrix least-squares methods on F^2, which converged to $R_F = 0.0642$ [$I > 2\sigma(I)$], 0.1944 (all data) and $Rw(F^2) = 0.1607$ [$I > 2\sigma(I)$], 0.1907 (all data). CCDC-211206 (**7**) and CCDC-211207 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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