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Novel Diethynylcarbazole Macrocycles: Synthesis and Optoelectronic Properties

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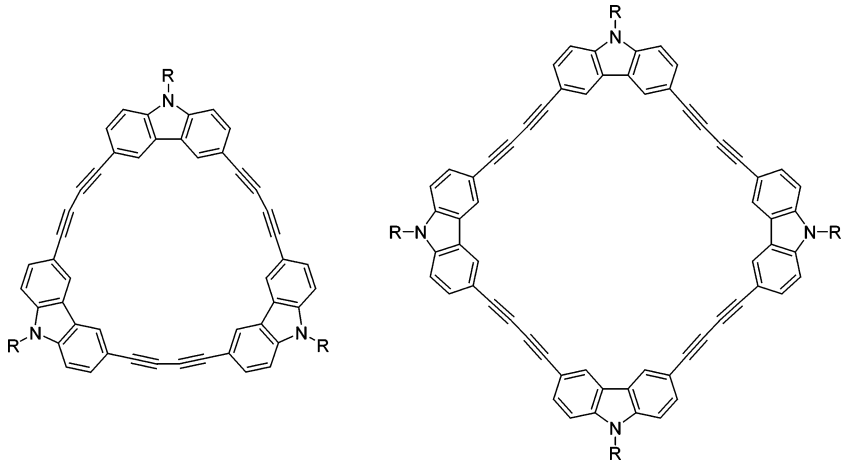

Diethynylcarbazole macrocycles **1b** and **2b** have been synthesized by oxidative coupling of appropriate precursors. In particular, macrocycle **2b** was prepared by bimolecular Pd-catalyzed oxidative coupling in 35% isolated yield. The spectroscopic properties of these macrocycles and their precursors were measured in detail. The films of these macrocycles by the dipping method and the Langmuir−Blodgett technique were fabricated to study their photoinduced charge-transfer properties. A rapid and steady cathodic photocurrent of these films was produced in a three-electrode cell when irradiated with white light. A possible mechanism of the photoinduced electron-transfer pathway was suggested.

Introduction

Shape-persistent macrocycles based on arylene, arylene ethynylene, and arylene butadiynylene backbones have currently attracted increasing attention due to their wide applications in the fields of supramolecular chemistry and materials science.[1] On one hand, they can form various supramolecular assemblies, such as extended tubular channels,[2] discotic liquid crystals,[3] and host−guest complexes,[4] because their molecular backbone is highly rigid and their internal cavity is in the nanometer scale. Especially, cyclic paraphenyleneacetylenes can form inclusion complexes with fullerenes.[5] On the other hand, because of the well-ordered structures and infinite conjugation of these macrocycles, they have interesting optical, electronic, and magnetic properties and can be ideal materials in organic conductors, organic field-effect transistors (OFETs), nonlinear optics (NLOs), and organic solar cells and so on.[6] To the best of our knowledge,

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(1) For recent reviews on shape-persistent macrocycles, see: (a) Moore, J. S. *Acc. Chem. Res.* **1997**, *30*, 402−413. (b) Höger, S. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2685−2698. (c) Haley, M. M.; Pak, J. J.; Brand, S. C. *Top. Curr. Chem.* **1999**, *201*, 81−130. (d) Grave, C.; Schlüter, A. D. *Eur. J. Org. Chem.* **2002**, 3075−3098. (e) Zhao, D.; Moore, J. S. *Chem. Commun.* **2003**, 807−818. (f) Yamaguchi, Y.; Yoshida, Z. I. *Chem.−Eur. J.* **2003**, *9*, 5430−5440. (g) Höger, S. *Chem.−Eur. J.* **2004**, *10*, 1320−1329. (h) *Acetylene Chemistry*; Diederich, F., Stang, P. J., Tykwinsky, R. R., Eds.; Wiley-VCH: Weinheim, 2005. (i) Höger, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 2−4.

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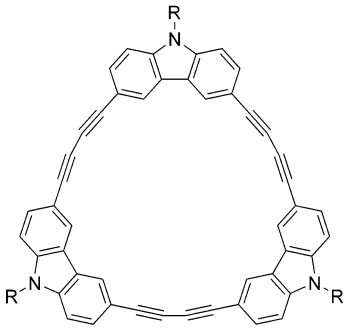
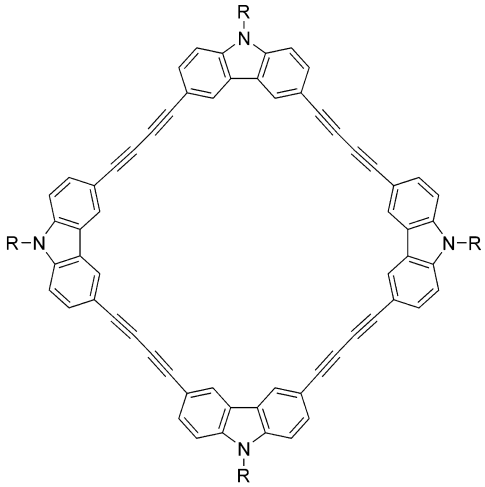
CHART 1. Diethynylcarbazole Macrocycles



1a: R = nC_4H_9
1b: R = $nC_{16}H_{33}$



2a: R = nC_4H_9
2b: R = $nC_{16}H_{33}$

most efforts have been made to investigate their self-association behaviors so far.[1−5] However, their optical and electronic properties have been barely studied.[6]

Recently, photoinduced electron transfer has generated much interest for the conversion of solar energy into chemical potential.[7−10] Donor−acceptor linked molecules or equivalents are used to mimic the charge-separation function of the natural photosynthetic reaction center and to study their potential use in solar cells. It has been proved that highly ordered molecular packing is crucial to efficient electron transfer.[11] Therefore, there is more and more interest in the synthesis of novel molecules with well-defined structures, such as macrocycles, dendrimers, and star-shaped architectures.[12,13] From this point of view, shape-persistent macrocycles are of great interest due to their aggregation behaviors and high degree of π conjugation.

The carbazole unit has fine optical and electronic properties as well as chemical stability due to its full aromaticity.[14] Therefore, it has been recently studied in a variety of fields including organic light-emitting diodes (OLEDs),[15] NLOs,[16] and OFETs.[17] Furthermore, the carbazole unit has been used as an electron-donating and chromophoric unit in the study of photoinduced electron transfer.[18] As far as we know, early research on carbazole-based macrocycles mainly concentrated on their synthesis;[6a,6d,19] however, the optical and electronic properties of these macrocycles were scarcely studied. Hence, we planned to synthesize the diethynylcarbazole macrocycle donors **1a**, **1b**, **2a**, and **2b** as well as study their self-association behaviors and optoelectronic properties (Chart 1). The buta-1,3-diyne unit was selected for the following reasons. It can be converted to thiophene,[6b] which is most frequently investigated as a result of its chemical stability in various redox states, easy functionalization, and extraordinary electronic properties.[20] Moreover, buta-1,3-diyne derivatives can pack in a highly ordered state by $\pi-\pi$ stacking and other noncovalent interactions and then undergo topochemically controlled polymerization to form polydiacetylenes,[21] which have interesting optical, electronic, and chromatic properties.[22]

To investigate their photoelectrochemical properties, the dipping method and Langmuir−Blodgett (LB) technique were employed to construct light−current conversion systems comprising the donors **1b** or **2b** and phenyl C_{61} butyric acid methyl

(2) (a) Venkataraman, D.; Lee, S.; Zhang, J.; Moore, J. S. *Nature* **1994**, *371*, 591−593. (b) Henze, O.; Lentz, D.; Schlüter, A. D. *Chem.−Eur. J.* **2000**, *6*, 2362−2367. (c) Hosokawa, Y.; Kawase, T.; Oda, M. *Chem. Commun.* **2001**, 1948−1949. (d) Höger, S.; Morrison, D. L.; Enkelmann, V. *J. Am. Chem. Soc.* **2002**, *124*, 6734−6736. (e) Henze, O.; Lentz, D.; Schäfer, A.; Franke, P.; Schlüter, A. D. *Chem.−Eur. J.* **2002**, *8*, 357−365. (f) Grave, C.; Lentz, D.; Schäfer, A.; Samori, P.; Rabe, J. P.; Franke, P.; Schlüter, A. D. *J. Am. Chem. Soc.* **2003**, *125*, 6907−6918.

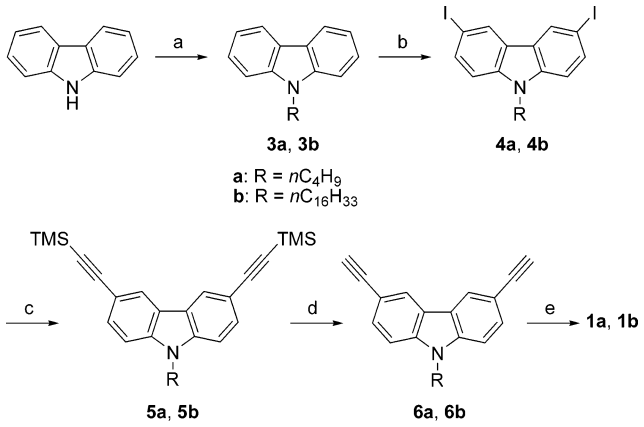
(3) (a) Zhang, J.; Moore, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 2655−2656. (b) Mindyuk, O. Y.; Stetzer, M. R.; Heiney, P. A.; Nelson, J. C.; Moore, J. S. *Adv. Mater.* **1998**, *10*, 1363−1366. (c) Höger, S.; Enkelmann, V.; Bonrad, K.; Tschierke, C. *Angew. Chem., Int. Ed.* **2000**, *39*, 2268−2270. (d) Höger, S.; Cheng, X. H.; Ramminger, A. D.; Enkelmann, V.; Rapp, A.; Mondeshki, M.; Schnell, I. *Angew. Chem., Int. Ed.* **2005**, *44*, 2801−2805.

(4) (a) Tobe, Y.; Utsumi, N.; Nagano, A.; Naemura, K. *Angew. Chem., Int. Ed.* **1998**, *37*, 1285−1287. (b) Tobe, Y.; Nagano, A.; Kawabata, K.; Sonoda, M.; Naemura, K. *Org. Lett.* **2000**, *2*, 3265−3268. (c) Sun, S.-S.; Lees, A. J. *Organometallics* **2001**, *20*, 2353−2358. (d) Baxter, P. N. W. *Chem.−Eur. J.* **2003**, *9*, 2531−2541. (e) Baxter, P. N. W. *Chem.−Eur. J.* **2003**, *9*, 5011−5022. (f) Venturi, M.; Marchioni, F.; Balzani, V.; Opris, D. M.; Henze, O.; Schlüter, A. D. *Eur. J. Org. Chem.* **2003**, 4227−4233. (g) Kobayashi, S.; Yamaguchi, Y.; Wakamiya, T.; Matsubara, Y.; Sugimoto, K.; Yoshida, Z. *Tetrahedron Lett.* **2003**, *44*, 1469−1472. (h) Yamaguchi, Y.; Kobayashi, S.; Miyamura, S.; Okamoto, Y.; Wakamiya, T.; Matsubara, Y.; Yoshida, Z. *Angew. Chem., Int. Ed.* **2004**, *43*, 366−369. (i) Kalsani, V.; Ammon, H.; Jäckel, F.; Rabe, J. P.; Schmittel, M. *Chem.−Eur. J.* **2004**, *10*, 5481−5492. (j) Baxter, P. N. W. *J. Org. Chem.* **2004**, *69*, 1813−1821. (k) Baxter, P. N. W.; Youcef, R. D. *J. Org. Chem.* **2005**, *70*, 4935−4953. (l) Chang, K.-J.; Moon, D.; Lah, M. S.; Jeong, K.-S. *Angew. Chem., Int. Ed.* **2005**, *44*, 1−5.

(5) (a) Kawase, T.; Seirai, Y.; Darabi, H. R.; Oda, M.; Sarakai, Y.; Tashiro, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 1621−1624. (b) Kawase, T.; Tanaka, K.; Fujiwara, N.; Darabi, H. R.; Oda, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 1624−1628. (c) Kawase, T.; Tanaka, K.; Seirai, Y.; Shiono, N.; Oda, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 5597−5600. (d) Gallant, A. J.; MacLachlan, M. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 5307−5310. (e) Kawase, T.; Tanaka, K.; Shiono, N.; Seirai, Y.; Oda, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 1722−1724. (f) Kawase, T.; Fujiwara, N.; Tsutumi, M.; Oda, M.; Maeda, Y.; Wakahara, T.; Akasaka, T. *Angew. Chem., Int. Ed.* **2004**, *43*, 5060−5062.

(6) (a) Maruyama, S.; Hokari, H.; Tao, X. T.; Gunji, A.; Wada, T.; Sasabe, H. *Chem. Lett.* **1999**, 731−732. (b) Krömer, J.; Rios-Carreras, I.; Fuhrmann, G.; Musch, C.; Wunderlin, M.; Debaerdemaeker, T.; Mena-Osteritz, E.; Bäuerle, P. *Angew. Chem., Int. Ed.* **2000**, *39*, 3481−3486. (c) Mena-Osteritz, E.; Bäuerle, P. *Adv. Mater.* **2001**, *13*, 243−246. (d) Maruyama, S.; Hokari, H.; Wada, T.; Sasabe, H. *Synthesis* **2001**, 1794−1799. (e) Mayor, M.; Didschies, C. *Angew. Chem., Int. Ed.* **2003**, *42*, 3176−3179. (f) Xu, H.; Yu, G.; Xu, W.; Xu, Y.; Cui, G.; Zhang, D.; Liu, Y.; Zhu, D. *Langmuir* **2005**, *21*, 5391−5395. (g) Marsden, J. A.; Miller, J. J.; Shirtcliff, L. D.; Haley, M. M. *J. Am. Chem. Soc.* **2005**, *127*, 2464−2476. (h) Marsden, J. A.; Haley, M. M. *J. Org. Chem.* **2005**, *70*, 10213−10226. (i) Mena-Osteritz, E.; Bäuerle, P. *Adv. Mater.* **2006**, *18*, 447−451.

SCHEME 1. Synthesis of Diethynylcarbazole Macrocycles 1a and 1b[a]



[a] (a) RBr, TBAI, NaOH, benzene. **3a**: 89%. **3b**: 91%. (b) NIS, AcOH, $CHCl_3$, room temperature, 6 h. **4a**: 92%. **4b**: 94%. (c) (Trimethylsilyl)-acetylene, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, THF, room temperature, 48 h. **5a**: 92%. **5b**: 93%. (d) NaOH, EtOH, room temperature, 1 h. **6a**: 90%. **6b**: 90%. (e) CuCl, $CuCl_2$, pyridine, room temperature, 72 h. **1b**: 6%.

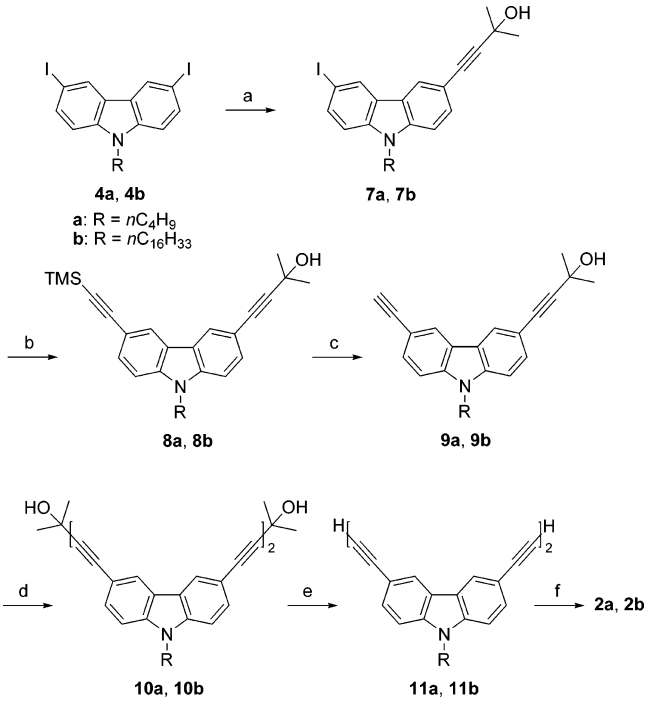
ester (PCBM), which is a soluble fullerene derivative and three-dimensional acceptor that has been widely used as a component of efficient electron-transfer systems due to its ability to give rise to rapid photoinduced charge separation and further slow charge recombination.[23,24]

Results and Discussion

Synthesis of 1a, 1b, 2a, and 2b. Target structures of our synthesis are macrocycles **1a**, **1b**, **2a**, and **2b** (Chart 1). The alkyl substituents were introduced to increase the solubility and adjust the association behaviors. In addition, macrocycles containing three or four carbazole units were synthesized to investigate the size effect on their optical and electronic properties. The one-pot oxidative coupling of the bisacetylenic precursors with one carbazole unit was adopted first because the starting materials were easily available and the trimer **1a** and tetramer **2a** or **1b** and **2b** could be prepared in one step.[25] The synthetic route is shown in Scheme 1.

Alkylation of a carbazole with 1-bromobutane and 1-bromohexadecane using tetrabutylammonium iodine as a phase-transfer catalyst gave **3a** and **3b** in 89% and 91% yield, respectively. **3a** and **3b** were then converted to the corresponding diiodo compounds **4a** (92%) and **4b** (94%) by *N*-iodosuccinimide (NIS). Palladium-catalyzed Sonogashira−Hagihara coupling of **4a** and **4b** (1.0 equiv) with (trimethylsilyl)acetylene (3.0 equiv) afforded **5a** and **5b** in 92% and 93% yield, respectively. Subsequently, deprotection of the trimethylsilyl group by aqueous NaOH gave the corresponding bisacetylenic compounds **6a** (90%) and **6b** (90%). Cyclization of **6b** with CuCl and $CuCl_2$ in pyridine under N_2 afforded a mixture of **1b** and **2b**, which had similar R_f values and could be only separated by preparative HPLC. **1b** was prepared in 6% isolated yield, whereas **2b** could only be detected by MALDI-TOF mass spectroscopy. However, it was not possible to isolate **1a** by a similar procedure because of its low solubility, although it was possible to detect the desired product by MALDI-TOF mass spectroscopy in the raw materials.

SCHEME 2. Synthesis of Diethynylcarbazole Macrocycles 2a and 2b[a]



[a] (a) 2-Methyl-3-butyn-2-ol, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, THF, room temperature, 5 h. **7a**: 49%. **7b**: 49%. (b) (Trimethylsilyl)acetylene, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, THF, room temperature, 52 h. **8a**: 95%. **8b**: 97%. (c) NaOH, MeOH, THF, room temperature. **9a**: 78%. **9b**: 95%. (d) **10a**: CuCl, $Cu(OAc)_2 \cdot H_2O$, pyridine, 60 °C, 19 h, 80%. **10b**: $Cu(OAc)_2 \cdot H_2O$, pyridine, 50 °C, 10 h, 80%. (e) KOH, MeOH, toluene, refluxing, 6 h. **11a**: 96%. **11b**: 96%. (f) $Pd(PPh_3)_2Cl_2$, CuI, I_2, iPr_2NH, THF, 50 °C. **2b**: 35%.

Because the yield was very low and the purification of the target macrocycles was extremely difficult in the first procedure, the cyclization reaction of two larger precursors with two carbazole units by intermolecular oxidative coupling ("half rings") was then employed to improve the yield and make the purification of the target compounds easier (Scheme 2).[1]

(7) (a) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435−461. (b) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **2001**, *34*, 40−48.

(8) (a) Yamazaki, T.; Yamazaki, I.; Osuka, A. *J. Phys. Chem. B* **1998**, *102*, 7858−7865. (b) Tkachenko, N. V.; Vuorimaa, E.; Kesti, T.; Alekseev, A. S.; Tauber, A. Y.; Hynninen, P. H.; Lemmetyinen, H. *J. Phys. Chem. B* **2000**, *104*, 6371−6379. (c) Guldi, D. M.; Zilbermann, I.; Anderson, G. A.; Kordatos, K.; Prato, M.; Tafuroc, R.; Valli, L. *J. Mater. Chem.* **2004**, *14*, 303−309. (d) Vuorinen, T.; Kaunisto, K.; Tkachenko, N. V.; Efimov, A.; Lemmetyinen, H. *Langmuir* **2005**, *21*, 5383−5390.

(9) (a) Yamada, H.; Imahori, H.; Nishimura, Y.; Yamazaki, I.; Fukuzumi, S. *Adv. Mater.* **2002**, *14*, 892−895. (b) Morisue, M.; Yamatsu, S.; Haruta, N.; Kobuke, Y. *Chem.−Eur. J.* **2005**, *11*, 5563−5574. (c) Cho, Y.-J.; Ahn, T. K.; Song, H.; Kim, K. S.; Lee, C. Y.; Seo, W. S.; Lee, K.; Kim, S. K.; Kim, D.; Park, J. T. *J. Am. Chem. Soc.* **2005**, *127*, 2380−2381. (d) Li, Y.; Liu, Y.; Wang, N.; Li, Y.; Liu, H.; Lu, F.; Zhuang, J.; Zhu, D. *Carbon* **2005**, *43*, 1968−1975.

(10) Li, H.; Li, Y.; Zhai, J.; Cui, G.; Liu, H.; Xiao, S.; Liu, Y.; Lu, F.; Jiang, L.; Zhu, D. *Chem.−Eur. J.* **2003**, *9*, 6031−6038.

(11) (a) Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. J. *Chem. Rev.* **2005**, *105*, 1491−1546. (b) Grimsdale, A. C.; Müllen, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 5592−5629.

(12) Choi, M.-S.; Yamazaki, T.; Yamazaki, I.; Aida, T. *Angew. Chem., Int. Ed.* **2004**, *43*, 150−158.

(13) Weil, T.; Reuther, E.; Müllen, K. *Angew. Chem., Int. Ed.* **2002**, *41*, 1900−1904.

(14) Morin, J.-F.; Leclerc, M.; Adès, D.; Siove, A. *Macromol. Rapid Commun.* **2005**, *26*, 761−778.

(15) (a) Brunner, K.; Dijken, A.; Börner, H.; Bastiaansen, J. J. A. M.; Kiggen, N. M. M.; Langeveld, B. M. W. *J. Am. Chem. Soc.* **2004**, *126*, 6035−6042. (b) Li, J.; Liu, D.; Li, Y.; Lee, C.-S.; Kwong, H.-L.; Lee, S. *Chem. Mater.* **2005**, *17*, 1208−1212.

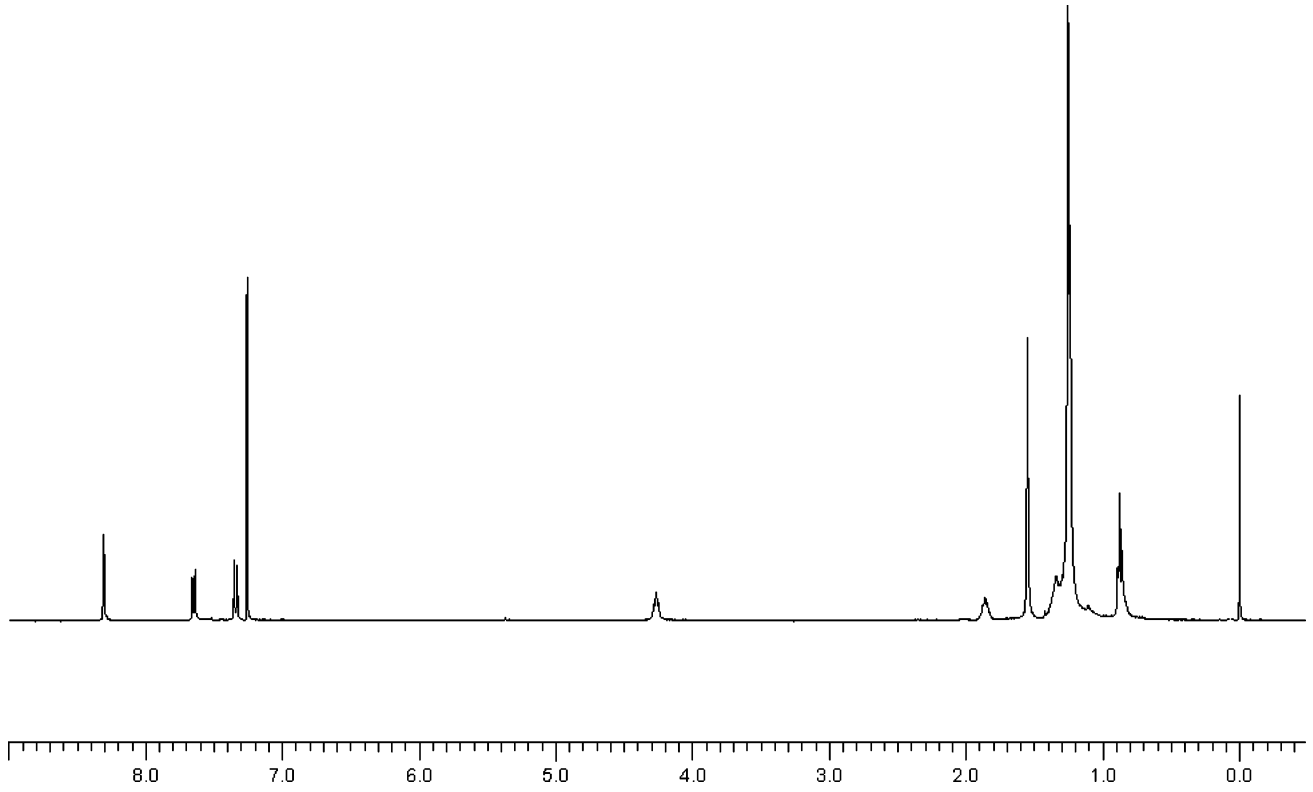


FIGURE 1. 400 MHz ^{1}H NMR spectra of macrocycle **2b**, recorded in $CDCl_3$ at 25 °C.

Palladium-catalyzed Sonogashira−Hagihara coupling of **4a** and **4b** (1.0 equiv) with 2-methyl-3-butyn-2-ol (roughly 1.0 equiv) gave **7a** (49%) and **7b** (49%), respectively. 2-Methyl-3-butyn-2-ol was used due to its high polarity which would facilitate the separation of the product from the starting materials and the bisethynylated byproduct. Subsequently, palladium-catalyzed coupling of **7a** and **7b** with (trimethylsilyl)acetylene gave **8a** (95%) and **8b** (97%), respectively. Because of the different cleavage kinetics of the trimethylsilyl and 2-hydroxypropan-2-yl groups, selective deprotection of the trimethylsilyl groups of **8a** and **8b** with aqueous NaOH at room temperature gave the corresponding monoprotected bisacetylenes **9a** (78%) and **9b** (95%). CuCl/$Cu(OAc)_2$·H_2O-promoted coupling of **9a** and $Cu(OAc)_2$·H_2O-promoted coupling of **9b** afforded **10a** (80%) and **10b** (80%), respectively, and subsequent deprotection of the 2-hydroxypropan-2-yl groups by NaOH under refluxing gave the corresponding bisacetylenic precursors **11a** (96%) and **11b** (96%). Because cyclization of **11b** by Cu-mediated oxidative coupling (CuCl/$CuCl_2$-promoted or CuCl/$Cu(OAc)_2$·H_2O-promoted) under pseudo high-dilution conditions gave no desired products, cyclization of **11b** by the Pd-catalyzed oxidative coupling in *i*-Pr_2NH and THF was employed to afford **2b** in 35% isolated yield. As for bimolecular cyclization, the yield was rather high.[26] Moreover, the purification of target compounds was much easier. This may be ascribed to the advantage of the Pd-catalyzed routine over the Cu-mediated procedure.[27] **2b** was characterized by NMR spectroscopy, IR spectroscopy, MALDI-TOF mass spectroscopy, and elemental analysis. The ^{1}H NMR spectra of **2b** show complete consumption of the raw materials and the high symmetry of the macrocycle (Figure 1). Unfortunately, it was not possible to isolate **2a** by a similar procedure because of its low solubility.

For comparison, intramolecular cyclization of one precursor with four carbazole units was also attempted (Scheme 3). Because of the low solubility of the butylcarbazoles, we only synthesized the hexadecylcarbazoles. Partial deprotection of **10b** under carefully controlled conditions gave the monoprotected bisacetylene **12** in 40% yield. Oxidative coupling of **12** with CuCl and $Cu(OAc)_2$·H_2O affored **13** in 80% yield, and subsequent deprotection gave the bisacetylene precursor **14** in 94% yield. Cyclization of **14** with CuCl and $CuCl_2$ in pyridine

(16) Zhang, Y.; Wada, T.; Sasabe, H. *J. Mater. Chem.* **1998**, *8*, 809−828.

(17) (a) Morin, J.-F.; Drolet, N.; Tao, Y.; Leclerc, M. *Chem. Mater.* **2004**, *16*, 4619−4626. (b) Wu, Y.; Li, Y.; Gardner, S.; Ong, B. S. *J. Am. Chem. Soc.* **2005**, *127*, 614−618. (c) Wu, Y.; Li, Y.; Gardner, S.; Ong, B. S. *Adv. Mater.* **2005**, *17*, 849−853. (d) Drolet, N.; Morin, J.-F.; Leclerc, N.; Wakim, S.; Tao, Y.; Leclerc, M. *Adv. Funct. Mater.* **2005**, *15*, 1671−1682.

(18) (a) Kawamura, K.; Aotani, Y.; Tomioka, H. *J. Phys. Chem. B* **2003**, *107*, 4579−4586. (b) Zhang, L.-P.; Chen, B.; Wu, L.-Z.; Tung, C.-H.; Cao, H.; Tanimoto, Y. *Chem.−Eur. J.* **2003**, *9*, 2763−2769. (c) Nakamura, Y.; Suzuki, M.; Imai, Y.; Nishimura, J. *Org. Lett.* **2004**, *6*, 2797−2799.

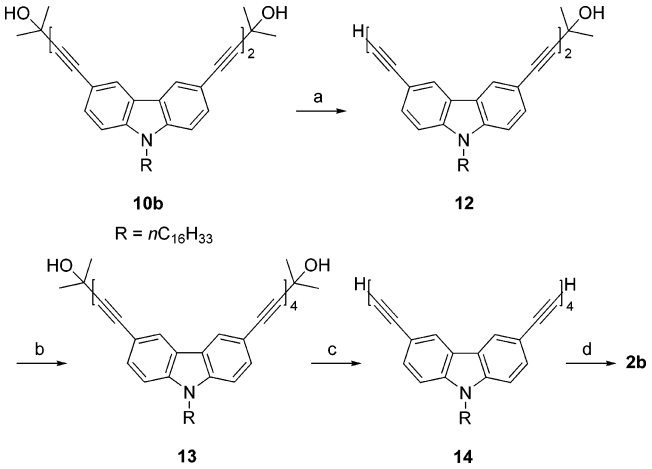
(19) (a) Zhang, W.; Moore, J. S. *J. Am. Chem. Soc.* **2004**, *126*, 12796. (b) Balakrishnan, K.; Datar, A.; Zhang, W.; Yang, X.; Naddo, T.; Huang, J.; Zuo, J.; Yen, M.; Moore, J. S.; Zang, L. *J. Am. Chem. Soc.* **2006**, *128*, 6576−6577.

(20) (a) Leclère, Ph.; Surin, M.; Viville, P.; Lazzaroni, R.; Kilbinger, A. F. M.; Henze, O.; Feast, W. J.; Cavallini, M.; Biscarini, F.; Schenning, A. P. H. J.; Meijer, E. W. *Chem. Mater.* **2004**, *16*, 4452−4466. (b) Barbarella, G.; Melucci, M.; Sotgiu, G. *Adv. Mater.* **2005**, *17*, 849−853.

(21) (a) Baldwin, K. P.; Matzger, A. J.; Scheiman, D. A.; Tessier, C. A.; Vollhardt, K. P. C.; Youngs, W. J. *Synlett* **1995**, 1215−1218. (b) Nomoto, A.; Sonoda, M.; Yamaguchi, Y.; Ichikawa, T.; Hirose, K.; Tobe, Y. *J. Org. Chem.* **2006**, *71*, 401−404.

(22) (a) Gan, H.; Liu, H.; Li, Y.; Zhao, Q.; Li, Y.; Wang, S.; Jiu, T.; Wang, N.; He, X.; Yu, D.; Zhu, D. *J. Am. Chem. Soc.* **2005**, *127*, 12452−12453. (b) Peng, H.; Tang, J.; Pang, J.; Chen, D.; Yang, L.; Ashbaugh, H. S.; Brinker, C. J.; Yang, Z.; Lu, Y. *J. Am. Chem. Soc.* **2005**, *127*, 12782−12783. (c) Kim, J.-M.; Lee, Y. B.; Yang, D. H.; Lee, J.-S.; Lee, G. S.; Ahn, D. J. *J. Am. Chem. Soc.* **2005**, *127*, 17580−17581.

SCHEME 3. Synthesis of Diethynylcarbazole Macrocycles 2b by Intramolecular Coupling[a]



[a] (a) KOH, MeOH, toluene, refluxing, 10 h, 40%. (b) CuCl, $Cu(OAc)_2 \cdot H_2O$, pyridine, 60 °C, 10 h, 80%. (c) KOH, MeOH, toluene, refluxing, 4.5 h, 94%. (d) CuCl, $CuCl_2$, pyridine, room temperature, 10%.

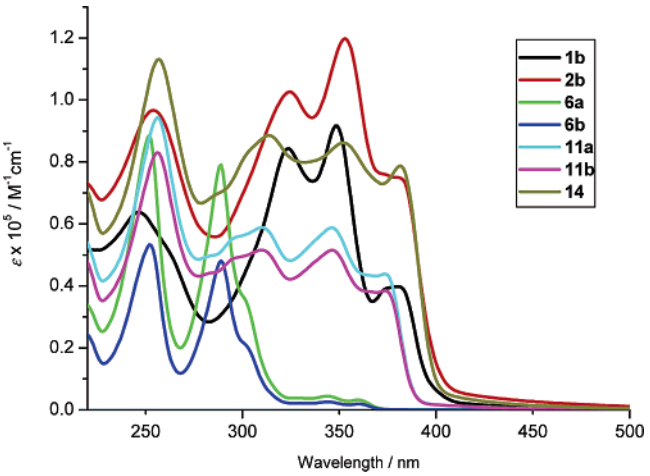


FIGURE 2. Normalized absorption spectra of macrocycles **1b** and **2b** and their precursors **6a**, **6b**, **11a**, **11b**, and **14** recorded in CH_2Cl_2 solution at room temperature.

exclusively afforded **2a** in 10% yield. The purification was more facile; however, preparation of the larger precursor requires more synthetic steps.

Optical Properties. The UV−vis absorption spectra of macrocycles **1b** and **2b** and their precursors **6a**, **6b**, **11a**, **11b**, and **14** are shown in Figure 2. The absorption spectra of macrocycles **1b** and **2b** were all composed of three low-energy absorption bands between 324 and 381 nm and the absorption maxima at 348−353 nm (Table 1). The absorption bands of tetramer **2b** closely matched those of trimer **1b** but were red shifted by 5 nm, which indicated the increment of the degree of π conjugation. All absorptions were invariant in energy and shape below 2.0×10^{-5} M in common solvents, such as CH_2Cl_2, THF, and toluene, showing that **1b** and **2b** were not aggregating in dilute solution. Compared with those of precursor **6b**, with one carbazole unit, the absorption spectra of trimer **1b** were largely red shifted by 59 nm, which implied that π conjugation length was significantly increased. Moreover, in comparison with that of precursor **11b**, with two carbazole units, the absorption maximum of tetramer **2b** was bathochromically shifted 7 nm, showing that the π conjugation length was increased to some extent. The UV−vis spectrum of butyl carbazole **11a** was similar to that of hexadecyl carbazole **11b** in energy, shape, and intensity, which indicated that the alkyl groups of the carbazole oligomers had no obvious impact on their UV−vis absorption properties. Furthermore, the absorption spectrum of the larger precursor **14** with four carbazole units was red shifted by 6 nm compared with that of precursor **11b** with two carbazole units.

TABLE 1. UV−Vis Data of Macrocycles and Their Precursors

compound	peak 1 λ_{max}/nm	peak 2 λ_{max}/nm	peak 3 λ_{max}/nm
1b	324	348	380
2b	324	353	381
6a	289	301	
6b	289	301	
11a	310	346	374
11b	310	346	374
14	314	352	381

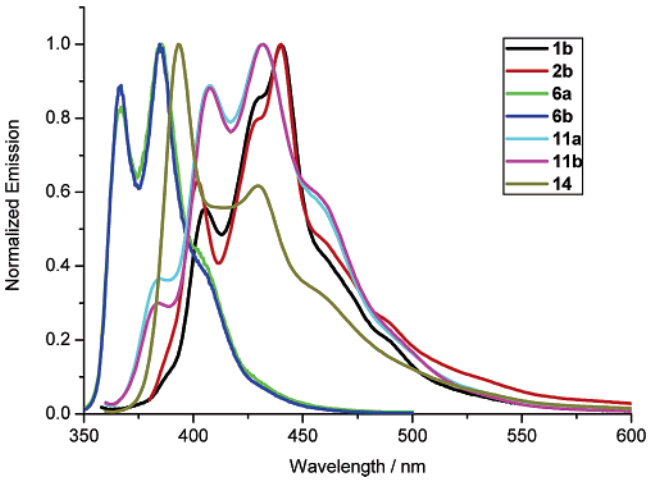


FIGURE 3. Normalized fluorescence emission spectra of macrocycles **1b** and **2b** and their precursors **6a**, **6b**, **11a**, **11b**, and **14** recorded in CH_2Cl_2 solution at room temperature.

The fluorescence emission spectra of macrocycles **1b** and **2b** and their precursors **6a**, **6b**, **11a**, **11b**, and **14** are shown in Figure 3. The fluorescence emission spectra of macrocycles **1b** and **2b** were virtually identical, consisting of a maximum emission at 440 nm and two shoulders at 402−405 and 428−429 nm (Table 2). The emission spectra of both precursors **6a** and **6b** with one carbazole unit were composed of two peaks at 366−367 and 385−386 nm, whereas the spectra of precursors **11a** and **11b** with two carbazole units all consisted of a sharp emission at 431−442 nm and two shoulders at 384−385 and 407−408 nm which indicated that alkyl groups had little influence on the excited-state energies of the precursors.

(23) (a) Martín, N.; Sánchez, L.; Illescas, B.; Pérez, I. *Chem. Rev.* **1998**, *98*, 2527−2547. (b) Echegoyen, L.; Echegoyen, L. E. *Acc. Chem. Res.* **1998**, *31*, 593−601. (c) Guldi, D. M.; Prato, M. *Acc. Chem. Res.* **2000**, *33*, 695−703.

(24) (a) Kim, K.-S.; Kang, M.-S.; Ma, H.; Jen, A. K.-J. *Chem. Mater.* **2004**, *16*, 5058−5062. (b) Liu, Y.; Wang, N.; Li, Y.; Liu, H.; Li, Y.; Xiao, J.; Xu, X.; Huang, C.; Cui, S.; Zhu, D. *Macromolecules* **2005**, *38*, 4880−4887. (c) Reyes-Reyes, M.; Kim, K.; Dewald, J.; López-Sandoval, R.; Avadhanula, A.; Curran, S.; Carroll, D. L. *Org. Lett.* **2005**, *7*, 5749−5752.

(25) (a) Staab, H. A.; Neunhoeffer, K. *Synthesis* **1974**, 424. (b) Traber, B.; Oeser, T.; Gleiter, R. *Eur. J. Org. Chem.* **2005**, 1283−1292.

(26) Opris, D. M.; Franke, P.; Schlüter, A. D. *Eur. J. Org. Chem.* **2005**, 822−837.

TABLE 2. Fluorescence Emission Data of Macrocycles and Their Precursors

compd	peak 1 λ_{max}/nm	peak 2 λ_{max}/nm	peak 3 λ_{max}/nm
1b	405	428	440
2b	402	429	440
6a	367	386	
6b	366	385	
11a	385	408	431
11b	384	407	432
14	393	429	

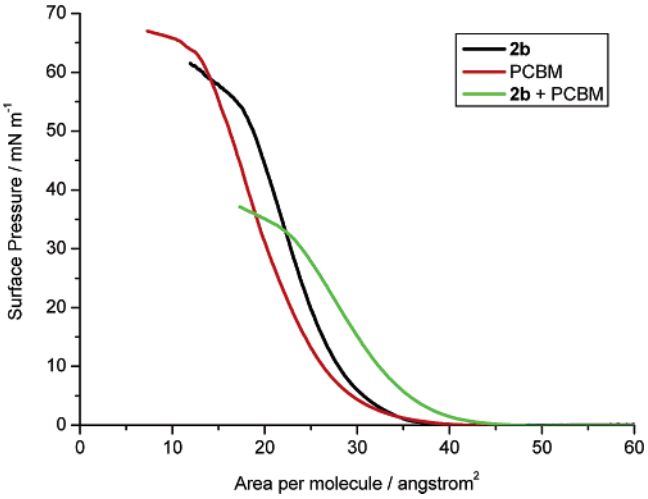


FIGURE 4. Surface pressure−area isotherms of **2b**, PCBM, and **2b**+PCBM at room temperature.

LB Films. Surface pressure−area isotherms (Π-*A*) of **2b**, PCBM, and **2b**+PCBM (the 1:1 mixture of **2b** and PCBM) are shown in Figure 4. **2b** formed a stable monolayer at the air−water interface, although it was not a typical amphiphilic molecule. The limiting area per molecule was extrapolated from the steepest part of the isotherm curve to the zero surface pressure. The limiting areas per molecule for the films of **2b** and PCBM were 29 and 27 Å^2, respectively. For the film of the mixture of **2b** and PCBM, the monolayer became unstable and collapsed at $\Pi > 32$ mN m^{-1}. This may result from the high propensity to aggregation of fullerene derivatives and phase separation between **2b** and PCBM.

The LB films of **2b** were transferred onto different substrates at the surface pressure of 15 mN m^{-1}. The transfer ratios were 1.0 ± 0.2. For the photoelectrical measurement, the film of the mixture of **2b** and PCBM (the **2b**+PCBM LB film) was transferred onto the ITO substrate at a surface pressure of 10 mN m^{-1}. The transfer ratios were 1.0 ± 0.2. For comparison, the film of PCBM was transferred onto the ITO substrate covered by the one-layer film of **2b** (the **2b**/PCBM LB film). At the surface pressure of 20 mN m^{-1}, the transfer ratios of PCBM were roughly 0.2. This was probably due to the strong interactions of PCBM.

The absorption spectra of **2b** in the LB film were measured to compare with those in the solution. As shown in Figure 5, the absorption spectrum of **2b** in the LB film was broadened and red shifted by 6 nm compared with that in the CH_2Cl_2 solution, indicating a side-by-side aggregation or J aggregation.[28]

(27) Marsden, J. A.; Miller, J. J.; Haley, M. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 1694−1697.

(28) Bouchard, J.; Belletête, M.; Durocher, G.; Leclerc, M. *Macromolecules* **2003**, *36*, 4624−4630.

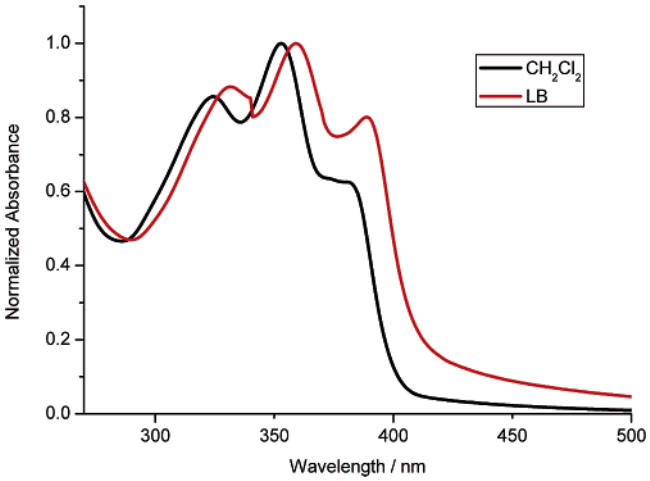


FIGURE 5. Normalized absorption spectra of **2b** in CH_2Cl_2 solution and in the six-layer LB film at room temperature.

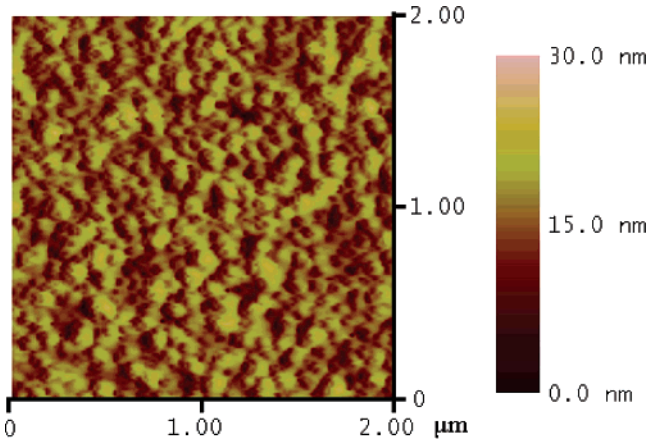


FIGURE 6. AFM images (2.00 × 2.00 μm) of the one-layer film of **2b** on mica.

Atomic Force Microscopy (AFM). The morphology of the LB films of **2b** was investigated by atomic force microscopy (AFM) (Figure 6). The one-layer film of **2b** deposited on mica was measured. The large square image (2.00 × 2.00 μm) showed that the film was extremely uniform. The height between the highest and the deepest parts of the film was roughly 17.0 nm, indicating that **2b** was aggregated to a certain extent.

Photocurrent Generation. The photocurrent was measured in an aqueous solution of 0.5 M KCl in a conventional three-electrode cell, using a modified ITO glass as a working electrode, a platinum wire as a counter electrode, and a saturated calomel electrode as a reference electrode.

First, the ITO plates were immersed in the dichloromethane solution of **14**, **1b**, and **2b** for 2 h, respectively, and then dried (the dipping method) for the photoelectrochemical measurement because the procedure was easily carried out. All the solution concentrations were 1 mg mL^{-1}. Steady cathodic photocurrents of the **14**, **1b**, and **2b** films were 0.19, 0.13, and 0.38 μA cm^{-2} at the irradiation of 72 mW cm^{-2} white light, respectively (Figure 7). The photocurrent generation was prompt and reproducible during several on/off cycles of white light irradiation. The photocurrent of the tetramer **2b** film was two times larger than that of the trimer **1b** film, which indicates that the degree of π conjugation is enhanced as the number of the carbazole unit is increased. Moreover, the photocurrent of the

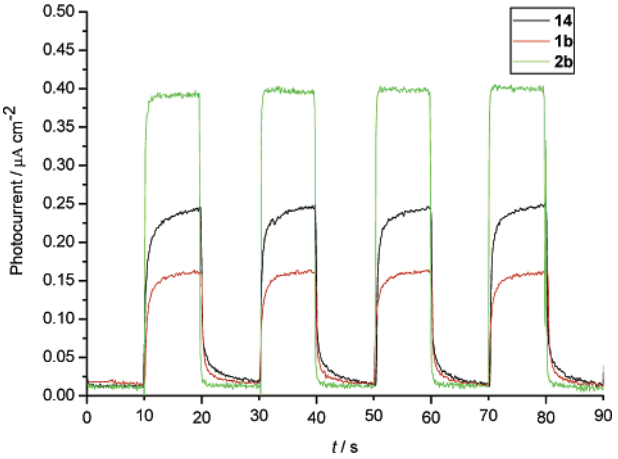


FIGURE 7. Photocurrent response of the **14**, **1b**, and **2b** films upon the irradiation of 72 mW cm^{-2} white light.

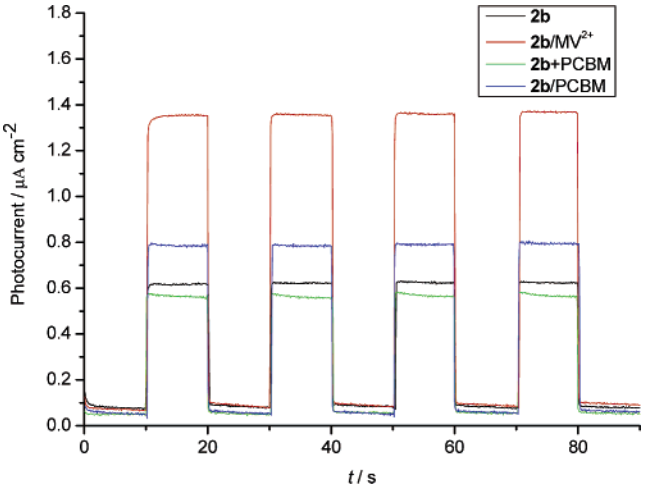


FIGURE 8. Photocurrent response of the **2b**, **2b**/MV^{2+}, **2b**+PCBM, and **2b**/PCBM LB films upon the irradiation of 72 mW cm^{-2} white light.

macrocycle **2b** film was two times as large as that of the linear precursor **14** film, which may be due to a large enhancement of the degree of π conjugation after cyclization.

For comparison, the LB film of **2b** was also prepared because the LB technique is an effective method to arrange molecules in highly ordered assemblies. When the ITO glass was modified with the one-layer film of **2b**, a steady 0.54 μA cm^{-2} cathodic photocurrent of the **2b** LB film was produced upon irradiation of 72 mW cm^{-2} white light (Figure 8). It was larger than that of the **2b** film prepared by the dipping method, showing that the ordering of molecules was improved. When methyl viologen (MV^{2+}, 0.05 M) was added in the KCl solution, a 1.28 μA cm^{-2} cathodic photocurrent of the **2b**/MV^{2+} LB film was rapidly produced, which was two times as large as that of the **2b** LB film without MV^{2+}. This phenomenon proved that electron carriers such as MV^{2+} could largely enhance the photocurrent. However, only a 0.52 μA cm^{-2} cathodic photocurrent of the **2b**+PCBM LB film (the LB film of the mixture of **2b** and PCBM) was observed, which was a little lower than that of the **2b** LB film without PCBM. This result was not expected because we considered that photoinduced electron transfer between the donor **2b** and the acceptor PCBM may increase the photocurrent. We ascribed this to strong interactions of

TABLE 3. Electrochemical Properties of Macrocycles 14, 1b, 2b, and PCBM[a]

compd	$E_{onset\ ox}$/V	$E_{onset\ red}$/V	E_{HOMO}/eV	E_{LUMO}/eV	E_g[b]/eV
14	1.16	−1.96[c]	−5.43	−2.31	3.12
1b	1.04	−2.10[c]	−5.31	−2.17	3.14
2b	1.10	−2.00[c]	−5.37	−2.27	3.10
PCBM		−0.58			

[a] Measured vs Ag wire. [b] E_g values were determined from UV−vis absorption spectra. [c] Calculated from the $E_{peak\ ox}$ and E_g.

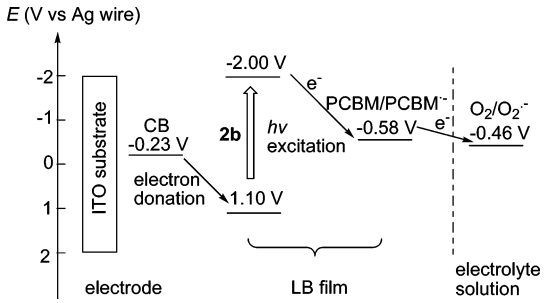


FIGURE 9. Schematic illustration of cathodic photocurrent generation.

PCBM as well as to phase separation between **2b** and PCBM. So, the **2b**/PCBM LB film was prepared, in which the films of **2b** and PCBM were deposited onto the ITO glass in succession. A steady 0.74 μA cm^{-2} cathodic photocurrent of the **2b**/PCBM LB film was produced, which was higher than that of the **2b** LB film without PCBM. By this means, photoinduced electron transfer between the donor **2b** and the acceptor PCBM was successfully realized.

Mechanism of Photoinduced Electron Transfer. To understand the electron-transfer process for the photocurrent generation, the energies of the relevant electronic states must be known. The relative HOMO and LUMO energies of **14**, **1b**, **2b**, and PCBM could be determined by cyclic voltammetry and UV−vis absorption spectroscopy. Because the oxidation and reduction processes correspond to the removal of electrons from the HOMO band and the filling of electrons into the LUMO band, respectively, the HOMO and LUMO energies have close relationships with the onset oxidation and reduction potentials, respectively. The onset oxidation potentials of **14**, **1b**, and **2b** were at 1.16, 1.04, and 1.10 V vs Ag wire, respectively (Table 3). The LUMO levels of **14**, **1b**, **2b**, and PCBM were at −1.96, −2.10, −2.00, and −0.58 V vs Ag wire, respectively. The energy of the conduction band of ITO is estimated as −4.5 eV (roughly −0.23 eV vs Ag wire).[10]

The photoinduced electron-transfer pathway of the **2b**/PCBM film is shown in Figure 9 as an example. First, electrons transfer from the conduction band (CB) of the ITO substrate to the macrocycle layer. Upon illumination, excitons form in this layer. Then, electrons transfer from **2b** to PCBM and form a charge-separated state. Last, the $PCBM^{\bullet-}$ moiety in the charge-separated state affords electron−electron carriers such as O_2 (−0.46 V vs Ag wire) or MV^{2+} (−0.60 V vs Ag wire) in the electrolyte solution. In a word, electrons flow from the ITO substrate through the LB film to the electrolyte solution and form the observed cathodic photocurrent.

The fluorescence quenching experiment can also reflect the electron-transfer process. Although the absorption spectrum of the mixture of **2b** and PCBM was similar to the sum of the respective spectra of **2b** and PCBM which indicated that no new complex was formed between **2b** and PCBM in the ground

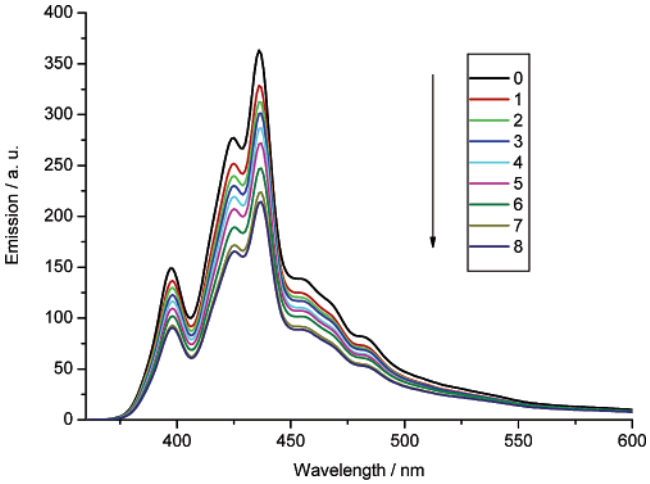


FIGURE 10. Fluorescence emission spectra of **2b** (1.0×10^{-5} M) in toluene with increasing concentration of PCBM ($\times 10^{-6}$ M): 0.0 (0), 1.0 (1), 2.0 (2), 3.0 (3), 4.0 (4), 5.0 (5), 6.0 (6), 7.0 (7), 8.0 (8). Excitation wavelength was 350 nm.

state, the fluorescence of **2b** was gradually quenched as the concentration of PCBM was increased (Figure 10). This indicated that electron transfer from photoexcited **2b** to PCBM might occur in the excited state. Furthermore, the dependence of the fluorescence intensity of **2b** on the concentration of PCBM follows the Stern−Volmer equation (eq 1), in which F_0 and F are the fluorescence intensity of **2b** without and with PCBM, respectively, K_{sv} is the quenching constant, and [Q] is the concentration of PCBM. The K_{sv} value was 7.02×10^4 M^{-1}. In the **2b**+PCBM or **2b**/PCBM thin films, the fluorescence was completely quenched (not shown).

$$F_0/F = 1 + K_{sv}[Q] \quad (1)$$

Conclusion

In conclusion, we have synthesized novel diethynylcarbazole macrocycles **1b** and **2b** by oxidative coupling. Especially, macrocycle **2b** was prepared by Pd-catalyzed oxidative coupling of two precursors in relatively high yield. The spectroscopic properties of these macrocycles and their precursors were measured. The light−current conversion properties of these macrocycles were studied in detail. The cathodic photocurrent response of these films was prompt, steady, and reproducible when irradiated upon white light. In particular, the photocurrent of the **2b** LB film was 1.28 μA cm^{-2} in the KCl solution using MV^{2+} as an electron carrier. The photoinduced electron transfer between macrocycle **2b** and PCBM was also investigated. Macrocycle **2b** exhibited an interesting fluorescence quenching response for PCBM, which indicated that electron transfer between the donor **2b** and the acceptor PCBM may take place in the excited state. This suggests that these macrocycles may be applied for organic solar cells.

Experimental Section

9-Butylcarbazole (3a). Carbazole (16.7 g, 100 mmol) was dissolved in benzene (20 mL). The phase-transfer catalyst tetrabutylammonium iodine (1.11 g, 3 mmol), 1-bromobutane (17.13 g, 125 mmol), and NaOH aqueous solution (50%, 120 mL) were added. The reaction mixture was heated to 80 °C and stirred for 2 h. The solvent was evaporated in vacuo, and the residue was extracted with dichloromethane. The organic layer was dried over Na_2SO_4 and filtered. After removal of the solvent, the product was recrystallized from ethanol to afford 9-butylcarbazole (**3a**) as a white solid (19.80 g, 89%). Mp 55−57 °C (lit.[29] mp 58 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.11 (d, ^3J = 7.8 Hz, 2H), 7.48−7.40 (m, 4H), 7.22 (t, ^3J = 7.3 Hz, 2H), 4.31 (t, ^3J = 7.2 Hz, 2H), 1.88−1.84 (m, 2H), 1.44−1.38 (m, 2H), 0.95 (t, ^3J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.5, 125.7, 122.9, 120.4, 118.8, 108.8, 42.9, 31.2, 20.7, 14.0. EI MS: *m*/*z* (%) 223 (50) [M^+], 180 (100) [$M^+ - C_4H_9$].

9-Hexadecylcarbazole (3b). Compound **3b** was prepared according to the procedure used for compound **3a**. **3b** was obtained as a white solid (91%). Mp 56−57 °C (lit.[30] mp 56.8−57.6 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.11 (d, ^3J = 7.7 Hz, 2H), 7.48−7.39 (m, 4H), 7.22 (t, ^3J = 7.4 Hz, 2H), 4.30 (t, ^3J = 7.2 Hz, 2H), 1.89−1.85 (m, 2H), 1.40−1.23 (m, 26H), 0.88 (t, ^3J = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.5, 125.7, 122.9, 120.4, 118.8, 108.8, 43.2, 32.1, 29.9, 29.83, 29.80, 29.76, 29.73, 29.66, 29.60, 29.57, 29.5, 29.1, 27.5, 22.9, 14.3. EI MS: *m*/*z* (%) 391 (100) [M^+], 180 (65) [$M^+ - C_{16}H_{33}$].

3,6-Diiodo-9-butylcarbazole (4a). A mixture of **3a** (2.23 g, 10 mmol) and *N*-iodosuccinimide (NIS) (5.4 g, 24 mmol) was stirred in chloroform (100 mL) and acetic acid (30 mL) at room temperature under N_2 for 6 h. The chloroform was evaporated in vacuo, and the residue was poured into water (200 mL). The mixture was extracted with dichloromethane. The organic layer was dried over $MgSO_4$ and filtered. Removal of the solvent followed by column chromatography on silica gel using petroleum ether as an eluent afforded **4a** as a light yellow solid (4.38 g, 92%). Mp 112−113 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.34 (s, 2H), 7.72 (d, ^3J = 8.6 Hz, 2H), 7.19 (d, ^3J = 8.5 Hz, 2H), 4.24 (t, ^3J = 7.1 Hz, 2H), 1.81 (m, 2H), 1.36−1.34 (m, 2H), 0.93 (t, ^3J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.4, 134.4, 129.2, 123.9, 110.9, 81.8, 42.9, 31.0, 20.5, 13.9. FT-IR (KBr): ν 3048, 2951, 2927, 2863, 1623, 1593, 1484, 1455, 1378, 1347, 1327, 1260, 1238, 1211, 1148, 873, 747 cm^{-1}. EI MS: *m*/*z* (%) 475 (100) [M^+]. HRMS (FAB, [M^+]) calcd for $C_{16}H_{15}I_2N$, 474.9288; found, 474.9285.

3,6-Diiodo-9-hexadecylcarbazole (4b). Compound **4b** was prepared according to the procedure used for compound **4a**. **4b** was obtained as a white solid (94%). Mp 85−86 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.33 (s, 2H), 7.72 (d, ^3J = 8.6 Hz, 2H), 7.18 (d, ^3J = 8.6 Hz, 2H), 4.22 (t, ^3J = 7.1 Hz, 2H), 1.81−1.79 (m, 2H), 1.29−1.22 (m, 26H), 0.88 (t, ^3J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.5, 134.5, 129.4, 124.0, 110.9, 81.8, 43.3, 32.1, 29.84, 29.81, 29.77, 29.72, 29.66, 29.57, 29.5, 29.4, 28.9, 27.3, 22.8, 14.3. FT-IR (KBr): ν 3059, 2921, 2848, 1601, 1513, 1468, 1429, 1347, 1312, 1285, 1230, 1149, 871, 797 cm^{-1}. EI MS: *m*/*z* (%) 643 (100) [M^+]. HRMS (FAB, [M^+]) calcd for $C_{28}H_{39}I_2N$, 643.1166; found, 643.1163.

3,6-Bis[(trimethylsilyl)ethynyl]-9-butylcarbazole (5a). To a flask containing $Pd(PPh_3)_2Cl_2$ (0.15 g, 0.21 mmol), CuI (0.062 g, 0.33 mmol), and **4a** (6.088 g, 12.8 mmol) were added (trimethylsilyl)acetylene (3.770 g, 38.4 mmol) in triethylamine (75 mL) and tetrahydrofuran (125 mL). The flask was then evacuated and backfilled with nitrogen three times. The mixture was stirred at room temperature under N_2 for 48 h and then filtered. The filtrate was concentrated and subjected to column chromatography on silica gel using petroleum ether as an eluent to afford **5a** as a yellow oil (4.87 g, 92%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.19 (s, 2H), 7.57 (d, ^3J = 8.2 Hz, 2H), 7.29 (d, ^3J = 8.5 Hz, 2H), 4.23 (t, ^3J = 7.2 Hz, 2H), 1.85−1.75 (m, 2H), 1.41−1.28 (m, 2H), 0.92 (t, ^3J = 7.3 Hz, 3H), 0.29 (s, 18H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 140.6, 129.9, 124.6, 122.2, 113.6, 108.8, 106.3, 91.9, 43.0, 30.9, 20.4, 13.7, 0.1. FT-IR (KBr): ν 3049, 2959, 2152 (C≡C), 1627, 1598,

(29) Buu-Hoï, NG. PH.; Royer, R. *J. Org. Chem.* **1951**, *16*, 1198−1205.
(30) Wang, X. D.; Zhang, B. W.; Bai, J. W.; Cao, Y.; Xiao, X. R.; Xu, J. M. *J. Phys. Chem.* **1992**, *96*, 2886−2891.

1482, 1457, 1381, 1352, 1286, 1249, 1207, 1150, 859, 759 cm^{-1}. EI MS: *m/z* (%) 415 (100) [M^+]. Anal. Calcd for $C_{26}H_{33}NSi_2$: C, 75.12; H, 8.00; N, 3.37. Found: C, 75.42; H, 8.03; N, 3.38.

3,6-Bis[(trimethylsilyl)ethynyl]-9-hexadecylcarbazole (5b). Compound **5b** was prepared according to the procedure used for compound **5a**. **5b** was obtained as a yellow oil (86%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.19 (s, 2H), 7.58−7.56 (m, 2H), 7.31 (d, ^3J = 8.5 Hz, 2H), 4.25 (t, ^3J = 7.2 Hz, 2H), 1.85−1.82 (m, 2H), 1.34−1.22 (m, 26H), 0.88 (t, ^3J = 7.0 Hz, 3H), 0.28 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.7, 130.1, 124.8, 122.5, 113.9, 108.9, 106.5, 92.2, 43.4, 32.1, 32.0, 29.84, 29.82, 29.78, 29.74, 29.68, 29.62, 29.52, 29.48, 29.0, 27.4, 22.9, 14.3, 0.3. FT-IR (KBr): ν 3057, 2957, 2926, 2855, 2152 (C≡C), 1626, 1601, 1482, 1380, 1352, 1286, 1249, 1205, 1150, 852, 759 cm^{-1}. EI MS: *m/z* (%) 585 (100) [M^+]. HRMS (FAB, [M^+]) calcd for $C_{38}H_{57}NSi_2$, 583.4024; found, 583.4027.

3,6-Diethynyl-9-butylcarbazole (6a). NaOH aqueous solution (1.9 M, 4 mL) was added to a stirred solution of **5a** (1.55 g, 3.72 mmol) in ethanol (148 mL). The mixture was stirred at room temperature under N_2 for 1 h and then diluted with diethyl ether and water. The phases were separated. The aqueous phase was washed with diethyl ether, and the combined organic phase was washed with saturated brine. The organic phase was dried over $MgSO_4$, and the solvent was removed. The residual material was purified by column chromatography on silica gel using petroleum ether as an eluent to give **6a** (0.91 g, 90%) as a light yellow solid. Mp 100−101 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.22 (s, 2H), 7.61 (d, ^3J = 8.5 Hz, 2H), 7.35 (d, ^3J = 8.5 Hz, 2H), 4.28 (t, ^3J = 7.2 Hz, 2H), 3.08 (s, 2H), 1.88−1.80 (m, 2H), 1.41−1.33 (m, 2H), 0.95 (t, ^3J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 140.5, 130.0, 124.6, 122.1, 112.6, 108.8, 84.7, 75.4, 42.9, 30.9, 20.4, 13.7. FT-IR (KBr): ν 3309, 3274, 3055, 2957, 2931, 2103 (C≡C), 1626, 1594, 1480, 1382, 1353, 1285, 1215, 1150, 1129, 880, 810 cm^{-1}. EI MS: *m/z* (%) 271 (58) [M^+], 228 (100) [$M^+ - C_3H_7$]. HRMS (FAB, [M^+]) calcd for $C_{20}H_{17}N$, 271.1356; found, 271.1356.

3,6-Diethynyl-9-hexadecylcarbazole (6b). Compound **6b** was prepared according to the procedure used for compound **6a**. **6b** was obtained as a light yellow solid (90%). Mp 47−48 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.22 (s, 2H), 7.61 (d, ^3J = 8.5 Hz, 2H), 7.34 (d, ^3J = 8.5 Hz, 2H), 4.27 (t, ^3J = 7.2 Hz, 2H), 3.07 (s, 2H), 1.88−1.81 (m, 2H), 1.32−1.22 (m, 26H), 0.88 (t, ^3J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.7, 130.2, 124.8, 122.3, 112.8, 109.0, 84.9, 75.6, 43.4, 32.1, 29.83, 29.81, 29.77, 29.73, 29.66, 29.59, 29.51, 29.45, 29.0, 27.3, 22.8, 14.3. FT-IR (KBr): ν 3291, 3056, 2921, 2849, 2103 (C≡C), 1628, 1600, 1482, 1379, 1352, 1289, 1230, 1151, 1129, 890, 813 cm^{-1}. EI MS: *m/z* (%) 439 (100) [M^+]. HRMS (FAB, [M^+]) calcd for $C_{32}H_{41}N$, 439.3234; found, 439.3227.

Macrocycle 1b. A solution of **6b** (0.439 g, 1 mmol) in pyridine (200 mL) was added slowly to a mixture of CuCl (9.9 g, 100 mmol) and $CuCl_2$ (2 g, 15 mmol) in pyridine (300 mL) under N_2 at room temperature. Upon completion of the slow addition (18 h), the reaction mixture was stirred for an additional 72 h. After removal of the solvent, the residual material was diluted with water, neutralized by diluent HCl solution, extracted with dichloromethane, washed with water, and dried over Na_2SO_4. The crude material was subjected to column chromatography on silica gel (petroleum ether/dichloromethane 1:1) and then purified by repetitive HPLC using chloroform as an eluent to afford **1b** as a yellow solid (0.026 g, 6%). Mp 125 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.44 (s, 6H), 7.57 (d, ^3J = 8.4 Hz, 6H), 7.35 (d, ^3J = 8.4 Hz, 6H), 4.31−4.27 (m, 6H), 1.88−1.86 (m, 6H), 1.35−1.24 (m, 78H), 0.87 (t, ^3J = 6.9 Hz, 9H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 140.8, 128.0, 127.7, 122.6, 112.9, 108.9, 84.0, 73.8, 43.5, 31.9, 29.71, 29.68, 29.6, 29.5, 29.47, 29.4, 29.0, 27.3, 22.7, 14.1. FT-IR (KBr): ν 3055, 2962, 2924, 2852, 2177 (C≡C), 2139 (C≡C), 2054, 1659, 1627, 1594, 1482, 1457, 1351, 1261 cm^{-1}. MALDI-TOF MS: *m/z* 1312.3 [M^+]. Anal. Calcd for $C_{96}H_{117}N_3$: C, 87.82; H, 8.98; N, 3.20. Found: C, 87.78; H, 9.01; N, 3.21.

Macrocycle 1a. Macrocycle **1a** was prepared according to the procedure used for macrocycle **1b**. However, it could not be isolated because of its poor solubility. MALDI-TOF MS: *m/z* 807 [M^+].

4-(6-Iodo-9-butylcarbazol-3-yl)-2-methylbut-3-yn-2-ol (7a). To a flask containing $Pd(PPh_3)_2Cl_2$ (0.14 g, 0.2 mmol), CuI (0.032 g, 0.17 mmol), and **4a** (4.75 g, 10 mmol) were added 2-methyl-3-butyn-2-ol (0.868 g, 10.3 mmol) in triethylamine (15 mL) and tetrahydrofuran (25 mL). The flask was then evacuated and backfilled with nitrogen three times. The mixture was stirred at room temperature under N_2 for 5 h and then filtered. The filtrate was concentrated and subjected to column chromatography on aluminum oxide (petroleum ether/dichloromethane 1:5) to afford **7a** as a light yellow solid (2.10 g, 49%). Mp 52−53 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.36 (d, ^5J = 1.4 Hz, 1H), 8.12 (d, ^5J = 0.8 Hz, 1H), 7.72−7.70 (m, 1H), 7.54−7.51 (m, 1H), 7.32 (d, ^3J = 8.5 Hz, 1H), 7.20 (d, ^3J = 8.6 Hz, 1H), 4.26 (t, ^3J = 7.1 Hz, 2H), 2.04 (s, 1H), 1.84−1.80 (m, 2H), 1.67 (s, 6H), 1.39−1.33 (m, 2H), 0.93 (t, ^3J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.9, 139.8, 134.2, 129.9, 129.3, 124.8, 124.2, 121.4, 113.3, 110.9, 108.8, 92.3, 83.0, 81.7, 65.8, 43.0, 31.8, 31.0, 20.5, 13.8. FT-IR (KBr): ν 3337 (br) (H−O-), 3059, 2959, 2930, 2870, 2224 (C≡C), 1624, 1591, 1564, 1479, 1437, 1375, 1348, 1284, 1241, 1120, 1151, 1018, 873, 802, 761 cm^{-1}. EI MS: *m/z* (%) 431 (32) [M^+]. HRMS (FAB, [M^+]) calcd for $C_{21}H_{22}INO$, 431.0741; found, 431.0740.

4-(6-Iodo-9-hexadecylcarbazol-3-yl)-2-methylbut-3-yn-2-ol (7b). Compound **7b** was prepared according to the procedure used for compound **7a**. **7b** was isolated as a light yellow solid (49%). Mp 72−73 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.36 (s, 1H), 8.11 (s, 1H), 7.72 (d, ^3J = 8.4 Hz, 1H), 7.53 (d, ^3J = 8.4 Hz, 1H), 7.32 (d, ^3J = 8.4 Hz, 1H), 7.19 (d, ^3J = 8.6 Hz, 1H), 4.24 (t, ^3J = 7.2 Hz, 2H), 2.03 (s, 1H), 1.85−1.79 (m, 2H), 1.66 (s, 6H), 1.36−1.22 (m, 26H), 0.88 (t, ^3J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.03, 139.99, 134.3, 130.0, 129.4, 125.0, 124.3, 121.5, 113.4, 111.0, 108.9, 92.3, 83.1, 81.8, 65.9, 43.4, 32.1, 31.8, 29.8, 29.71, 29.66, 29.58, 29.49, 29.45, 29.0, 27.3, 22.8, 14.3. FT-IR (KBr): ν 3353 (br) (H−O-), 3062, 2921, 2849, 2226 (C≡C), 1625, 1593, 1481, 1437, 1377, 1349, 1288, 1226, 1153, 1113, 1020, 872, 809, 788 cm^{-1}. EI MS: *m/z* (%) 599 (20) [M^+], 581 (100) [$M^+ - H_2O$]. HRMS (FAB, [M^+]) calcd for $C_{33}H_{46}INO$, 599.2619; found, 599.2613.

4-[6-(Trimethylsilyl)ethynyl-9-butylcarbazol-3-yl]-2-methylbut-3-yn-2-ol (8a). To a flask containing $Pd(PPh_3)_2Cl_2$ (0.14 g, 0.2 mmol), CuI (0.038 g, 0.2 mmol), and **7a** (4.31 g, 10 mmol) were added (trimethylsilyl)acetylene (2.07 g, 21.08 mmol) in triethylamine (15 mL) and tetrahydrofuran (25 mL). The flask was then evacuated and backfilled with nitrogen three times. The mixture was stirred at room temperature under N_2 for 52 h and then filtered. The filtrate was concentrated and subjected to column chromatography on silica gel (petroleum ether/dichloromethane 1:5) to afford **8a** as a yellow oil (3.82 g, 95%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.19 (s, 1H), 8.14 (s, 1H), 7.58 (d, ^3J = 8.5 Hz, 1H), 7.53 (d, ^3J = 8.5 Hz, 1H), 7.32−7.29 (m, 2H), 4.26 (t, ^3J = 7.2 Hz, 2H), 2.07 (s, 1H), 1.84−1.81 (m, 2H), 1.67 (s, 6H), 1.39−1.34 (m, 2H), 0.94 (t, ^3J = 7.3 Hz, 3H), 0.29 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.4, 140.3, 129.9, 129.7, 124.6, 124.1, 122.3, 122.2, 113.6, 113.3, 108.83, 108.76, 106.6, 92.2, 92.0, 83.1, 65.8, 42.9, 31.8, 31.0, 20.5, 13.8, 0.3. FT-IR (KBr): ν 3326 (br) (H−O-), 3051, 2960, 2933, 2901, 2873, 2222 (C≡C), 2150 (C≡C), 1628, 1600, 1568, 1484, 1457, 1379, 1354, 1286, 1248, 1212, 1151, 1067, 890, 852, 807, 759 cm^{-1}. EI MS: *m/z* (%) 401 (4) [M^+], 383 (100) [$M^+ - H_2O$]. HRMS (FAB, [M^+]) calcd for $C_{26}H_{31}NOSi$, 401.2169; found, 401.2165.

4-[6-(Trimethylsilyl)ethynyl-9-hexadecylcarbazol-3-yl]-2-methylbut-3-yn-2-ol (8b). Compound **8b** was prepared according to the procedure used for compound **8a**. **8b** was isolated as a yellow oil (97%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.19 (d, ^5J = 1.0 Hz, 1H), 8.14 (d, ^5J = 1.1 Hz, 1H), 7.58−7.56 (m, 1H), 7.53−7.51 (m, 1H), 7.32−7.29 (m, 2H), 4.25 (t, ^3J = 7.2 Hz, 2H), 2.05 (s, 1H), 1.83 (m, 2H), 1.67 (s, 6H), 1.31−1.22 (m, 26H), 0.88 (t, ^3J = 7.0 Hz,

3H), 0.29 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.6, 140.4, 130.1, 129.8, 124.7, 124.3, 122.4, 122.3, 113.8, 113.4, 108.93, 108.86, 106.6, 92.2, 92.1, 83.2, 65.9, 43.4, 32.1, 31.8, 29.8, 29.71, 29.65, 29.6, 29.49, 29.45, 29.0, 27.3, 22.8, 14.3, 0.3. FT-IR (KBr): ν 3356 (br) (H−O-), 3049, 2925, 2853, 2223 (C≡C), 2151 (C≡C), 1628, 1600, 1561, 1484, 1461, 1379, 1353, 1286, 1248, 1229, 1192, 1151, 1063, 888, 845, 806, 760 cm^{-1}. EI MS: *m*/*z* (%) 569 (14) [M^+], 551 (11) [$M^+ - H_2O$], 511 (100) [$M^+ - H_2O - C_3H_4$]. HRMS (FAB, [M^+]) calcd for $C_{38}H_{55}NOSi$, 569.4047; found, 569.4040.

4-[6-Ethynyl-9-butylcarbazol-3-yl]-2-methylbut-3-yn-2-ol (9a). NaOH aqueous solution (5.0 M, 4 mL) was added to a stirred solution of **8a** (4.01 g, 10 mmol) in tetrahydrofuran (15 mL) and methanol (20 mL). After complete consumption of the starting material (18 h), the reaction mixture was diluted with diethyl ether and water. The phases were separated. The aqueous phase was washed with diethyl ether, and the combined organic phase was washed with saturated brine. The organic phase was dried over $MgSO_4$, and the solvent removed. The residual material was purified by column chromatography on silica gel (petroleum ether/dichloromethane 1:5) to give **9a** (2.57 g, 78%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.21 (d, ^5J = 1.0 Hz, 1H), 8.15 (d, ^5J = 0.9 Hz, 1H), 7.59 (m, 1H), 7.54−7.52 (m, 1H), 7.34−7.32 (m, 2H), 4.27 (t, ^3J = 7.2 Hz, 2H), 3.08 (s, 1H), 2.08 (s, 1H), 1.84−1.82 (m, 2H), 1.67 (s, 6H), 1.38−1.36 (m, 2H), 0.94 (t, ^3J = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.4, 140.2, 129.9, 129.7, 124.6, 124.0, 122.2, 122.1, 113.3, 112.4, 108.8, 92.3, 84.9, 83.1, 75.5, 65.7, 42.8, 31.7, 30.9, 20.4, 13.8. FT-IR (KBr): ν 3357 (br) (H−O-), 3291 (H−C≡), 3053, 2960, 2931, 2871, 2224 (C≡C), 2102 (C≡C), 1628, 1599, 1568, 1484, 1457, 1379, 1354, 1286, 1239, 1212, 1151, 1133, 1067, 883, 808, 748 cm^{-1}. EI MS: *m*/*z* (%) 329 (7) [M^+], 268 (100) [$M^+ - H_2O - C_3H_7$]. HRMS (FAB, [M^+]) calcd for $C_{23}H_{23}NO$, 329.1774; found, 329.1774.

4-[6-Ethynyl-9-hexadecylcarbazol-3-yl]-2-methylbut-3-yn-2-ol (9b). Compound **9b** was prepared according to the procedure used for compound **9a**. **9b** was isolated as a yellow oil (95%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.21 (d, ^5J = 1.2 Hz, 1H), 8.15 (d, ^5J = 1.2 Hz, 1H), 7.61−7.59 (m, 1H), 7.54−7.52 (m, 1H), 7.34−7.31 (m, 2H), 4.26 (t, ^3J = 7.2 Hz, 2H), 3.08 (s, 1H), 2.04 (s, 1H), 1.84 (m, 2H), 1.67 (s, 6H), 1.31−1.22 (m, 26H), 0.88 (t, ^3J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.7, 140.4, 130.1, 129.9, 124.8, 124.3, 122.4, 122.3, 113.5, 112.6, 108.9, 92.3, 84.9, 83.2, 75.5, 65.9, 43.3, 32.0, 31.8, 29.8, 29.7, 29.65, 29.58, 29.48, 29.44, 29.0, 27.3, 22.8, 14.2. FT-IR (KBr): ν 3361 (br) (H−O-), 3311 (H−C≡), 3050, 2925, 2853, 2227 (C≡C), 2104 (C≡C), 1629, 1600, 1569, 1484, 1461, 1379, 1353, 1287, 1229, 1153, 1060, 883, 807, 725 cm^{-1}. EI MS: *m*/*z* (%) 497 (20) [M^+], 479 (40) [$M^+ - H_2O$], 439 (100) [$M^+ - H_2O - C_3H_4$]. HRMS (FAB, [M^+]) calcd for $C_{35}H_{47}NO$, 497.3652; found, 497.3648.

4,4′-[6,6′-(Buta-1,3-diyne-1,4-diyl)bis(9-butylcarbazole-6,3-diyl)]bis(2-methylbut-3-yn-2-ol) (10a). A solution of **9a** (1.077 g, 3.27 mmol) in pyridine (6 mL) was added to a suspension of CuCl (3.237 g, 32.7 mmol) and $Cu(OAc)_2 \cdot H_2O$ (6.529 g, 32.7 mmol) in pyridine (40 mL). The mixture was stirred at 60 °C for 19 h and then filtered. After removal of the solvent, the mixture was diluted with dichloromethane and water. The phases were separated. The organic layer was extracted with water. The combined organic layer was dried over $MgSO_4$ and filtered. The filtrate was concentrated and subjected to column chromatography on silica gel (ethyl acetate/petroleum ether 1:2) to afford **10a** as a light yellow solid (0.859 g, 80%). Mp 174−175 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.26 (s, 2H), 8.15 (s, 2H), 7.67−7.64 (m, 2H), 7.56−7.53 (m, 2H), 7.34 (t, ^3J = 8.3 Hz, 4H), 4.28 (t, ^3J = 7.2 Hz, 4H), 2.08 (s, 2H), 1.86−1.83 (m, 4H), 1.68 (s, 12H), 1.42−1.36 (m, 4H), 0.95 (t, ^3J = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.9, 140.6, 130.6, 130.0, 125.3, 124.4, 122.6, 122.4, 113.7, 112.6, 109.3, 109.1, 92.4, 83.2, 82.6, 73.1, 65.9, 43.3, 31.8, 31.2, 20.6, 14.0. FT-IR (KBr): ν 3331 (br) (H−O-), 3056, 2959, 2931, 2213 (C≡C), 2137 (C≡C), 1628, 1597, 1562, 1482, 1458, 1379, 1354, 1285, 1239, 1211, 1152, 879, 806, 745 cm^{-1}. MALDI-TOF MS: *m*/*z* 656.3 [M^+]. HRMS (FAB, [M^+]) calcd for $C_{46}H_{44}N_2O_2$, 656.3397; found, 656.3391.

4,4′-[6,6′-(Buta-1,3-diyne-1,4-diyl)bis(9-hexadecylcarbazole-6,3-diyl)]bis(2-methylbut-3-yn-2-ol) (10b). Compound **10b** was prepared according to the procedure used for compound **10a**. **10b** was isolated as a light yellow solid (80%). Mp 103−105 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.26 (s, 2H), 8.16 (s, 2H), 7.67 (d, ^3J = 8.4 Hz, 2H), 7.56 (d, ^3J = 8.4 Hz, 2H), 7.34 (t, ^3J = 8.4 Hz, 4H), 4.27 (t, ^3J = 6.9 Hz, 4H), 2.06 (s, 2H), 1.86−1.84 (m, 4H), 1.68 (s, 12H), 1.33−1.23 (m, 52H), 0.88 (t, ^3J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.7, 140.4, 130.4, 129.9, 125.1, 124.2, 122.5, 122.2, 113.6, 112.4, 109.1, 108.9, 92.4, 83.2, 82.6, 73.1, 65.8, 43.3, 32.0, 31.8, 29.79, 29.71, 29.65, 29.58, 29.5, 29.4, 29.0, 27.3, 22.8, 14.2. FT-IR (KBr): ν 3336 (br) (H−O-), 3056, 2924, 2852, 2222 (C≡C), 2140 (C≡C), 1628, 1597, 1566, 1483, 1380, 1352, 1286, 1232, 1151, 1133, 882, 806, 722 cm^{-1}. MALDI-TOF MS: *m*/*z* 992.7 [M^+]. HRMS (FAB, [M^+]) calcd for $C_{70}H_{92}N_2O_2$, 992.7153; found, 992.7142.

1,4-Bis(6-ethynyl-9-butylcarbazol-3-yl)buta-1,3-diyne (11a). KOH (0.034 g, 0.6 mmol) was added to a stirred solution of **10a** (0.131 g, 0.2 mmol) in methanol (2 mL) and toluene (20 mL). The mixture was refluxed for 6 h. And then it was diluted with dichloromethane and water. The phases were separated. The organic phase was dried over $MgSO_4$ and filtered. The filtrate was concentrated and purified by column chromatography on silica gel (petroleum ether/dichloromethane 1:1) to give **11a** (0.104 g, 96%) as a light yellow solid. Mp 70−72 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.28 (s, 2H), 8.24 (s, 2H), 7.68−7.61 (m, 4H), 7.38−7.34 (m, 4H), 4.30 (t, ^3J = 7.2 Hz, 4H), 3.09 (s, 2H), 1.87−1.84 (m, 4H), 1.43−1.37 (m, 4H), 0.96 (t, ^3J = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.9, 140.8, 130.6, 130.3, 125.3, 124.9, 122.5, 122.3, 113.0, 112.7, 109.2, 109.1, 84.8, 82.6, 75.7, 73.1, 43.2, 31.2, 20.6, 14.0. FT-IR (KBr): ν 3284 (H−O-), 3053, 2961, 2928, 2866, 2136 (C≡C), 2099 (C≡C), 1623, 1593, 1479, 1453, 1377, 1348, 1262, 1209, 1096, 1024, 876, 804, 749 cm^{-1}. MALDI-TOF MS: *m*/*z* 540.1 [M^+]. HRMS (FAB, [M^+]) calcd for $C_{40}H_{32}N_2$, 540.2560; found, 540.2562.

1,4-Bis(6-ethynyl-9-hexadecylcarbazol-3-yl)buta-1,3-diyne (11b). Compound **11b** was prepared according to the procedure used for compound **11a**. **11b** was isolated as a light yellow solid (96%). Mp 75−76 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.27 (d, ^5J = 1.1 Hz, 2H), 8.23 (s, 2H), 7.67−7.60 (m, 4H), 7.37−7.33 (m, 4H), 4.28 (t, ^3J = 7.2 Hz, 4H), 3.09 (s, 2H), 1.88−1.84 (m, 4H), 1.37−1.23 (m, 52H), 0.88 (t, ^3J = 7.1 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.9, 140.8, 130.6, 130.3, 125.3, 124.9, 122.5, 122.3, 113.0, 112.7, 109.2, 109.1, 84.9, 82.6, 75.7, 73.2, 43.5, 32.1, 29.8, 29.7, 29.69, 29.6, 29.52, 29.48, 29.0, 27.4, 22.8, 14.3. FT-IR (KBr): ν 3311 (H−C≡), 3288 (H−C≡), 3063, 2922, 2851, 2134 (C≡C), 2104 (C≡C), 1628, 1596, 1565, 1482, 1380, 1352, 1287, 1238, 1149, 1126, 884, 806, 722 cm^{-1}. MALDI-TOF MS: *m*/*z* 876.6 [M^+]. HRMS (FAB, [M^+]) calcd for $C_{64}H_{80}N_2$, 876.6316; found, 876.6322.

Macrocycle 2b. A solution of **11b** (0.175 g, 0.2 mmol) in tetrahydrofuran (50 mL) was added slowly to a suspension of $Pd(PPh_3)_2Cl_2$ (0.014 g, 0.02 mmol), CuI (0.0057 g, 0.03 mmol), and I_2 (0.025 g, 0.1 mmol) in diisopropylamine (200 mL) and tetrahydrofuran (200 mL) at 50 °C. Upon completion of the slow addition (21 h), the reaction mixture was stirred for an additional 12 h. After removal of the solvent and filtration, the residual material was recrystallized from dichloromethane to afford **2b** as a light yellow solid (0.062 g, 35%). Mp 120 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.31 (s, 8H), 7.66−7.64 (m, 8H), 7.35 (d, ^3J = 8.5 Hz, 8H), 4.27 (t, ^3J = 7.2 Hz, 8H), 1.88−1.85 (m, 8H), 1.34−1.24 (m, 104H), 0.88 (t, ^3J = 7.0 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.8, 130.4, 125.5, 122.5, 113.0, 109.2, 82.5, 73.3, 43.5, 32.1, 29.9, 29.8, 29.7, 29.6, 29.5, 29.1, 27.4, 22.9, 14.3. FT-IR (KBr): ν 2924, 2853, 2141 (C≡C), 2100 (C≡C), 1626, 1595, 1560, 1484, 1462, 1381, 1354, 1285, 1262, 1149, 1131, 1093, 879, 805,

737 cm^{-1}. MALDI-TOF MS: *m*/*z* 1750.6 [M^+]. Anal. Calcd for $C_{128}H_{156}N_4$: C, 87.82; H, 8.98; N, 3.20. Found: C, 87.86; H, 8.95; N, 3.19.

Macrocycle 2a. Macrocycle **2a** was prepared according to the procedure used for macrocycle **2b**. However, it could not be isolated because of its poor solubility. MALDI-TOF MS: *m*/*z* 1076.5 [M^+].

4-{6-[(6-Ethynyl-9-hexadecylcarbazol-3-yl)buta-1,3-diynyl]-9-hexadecylcarbazol-3-yl}-2-methylbut-3-yn-2-ol (12). KOH (0.51 g, 9.09 mmol) was added to a stirred solution of **10b** (0.099 g, 0.1 mmol) in methanol (5 mL) and toluene (15 mL). The mixture was refluxed for 10 h, and then it was diluted with dichloromethane and water. The phases were separated. The organic phase was dried over $MgSO_4$ and filtered. The filtrate was concentrated and purified by column chromatography on silica gel (petroleum ether/dichloromethane 1:5) to give **12** (0.037 g, 40%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.28−8.23 (m, 3H), 8.16 (s, 1H), 7.67−7.61 (m, 3H), 7.55 (d, ^3J = 8.5 Hz, 1H), 7.37−7.34 (m, 4H), 4.30−4.26 (m, 4H), 3.09 (s, 1H), 2.05 (s, 1H), 1.88−1.84 (m, 4H), 1.68 (s, 6H), 1.36−1.23 (m, 52H), 0.88 (t, ^3J = 7.1 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.9, 140.81, 140.77, 140.5, 130.6, 130.5, 130.3, 125.3, 125.2, 124.9, 124.3, 122.55, 122.49, 122.3, 113.6, 113.0, 112.7, 112.5, 109.23, 109.19, 109.1, 109.0, 92.3, 84.9, 83.2, 82.6, 82.5, 75.7, 73.2, 73.1, 65.9, 43.4, 32.1, 32.0, 31.8, 29.84, 29.81, 29.78, 29.73, 29.68, 29.61, 29.51, 29.47, 29.0, 27.4, 22.84, 22.80, 14.3. FT-IR (KBr): ν 3312 (H−O-), 3054, 2925, 2853, 2140 (C≡C), 2105 (C≡C), 1628, 1597, 1566, 1482, 1381, 1352, 1287, 1234, 1152, 1134, 884, 807, 723 cm^{-1}. MALDI-TOF MS: *m*/*z* 934.7 [M^+]. HRMS (FAB, [M^+]) calcd for $C_{67}H_{86}N_2O$, 934.6735; found, 934.6746.

4,4′-[6,6′-(6,6′-(Buta-1,3-diyne-1,4-diyl)bis(9-hexadecylcarbazole-3,6-diyl))]bis(buta-1,3-diyne-1,4-diyl)bis(9-hexadecylcarbazole-3,6-diyl)bis(2-methylbut-3-yn-2-ol) (13). A solution of **12** (0.067 g, 0.072 mmol) in pyridine (8 mL) was added to a suspension of CuCl (0.071 g, 0.72 mmol) and $Cu(OAc)_2 \cdot H_2O$ (0.144 g, 0.72 mmol) in pyridine (5 mL). The mixture was stirred at 60 °C for 10 h and then filtered. After removal of the solvent, the mixture was diluted with dichloromethane and water. The phases were separated. The organic layer was extracted with water. The combined organic layer was dried over $MgSO_4$ and filtered. The filtrate was concentrated and subjected to column chromatography on silica gel (petroleum ether/dichloromethane 1:5) to afford **13** as a yellow oil (0.054 g, 80%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.29 (d, ^3J = 9.9 Hz, 6H), 8.15 (s, 2H), 7.67 (t, ^3J = 8.2 Hz, 6H), 7.55 (d, ^3J = 8.4 Hz, 2H), 7.38−7.31 (m, 8H), 4.29−4.25 (m, 8H), 2.07 (s, 2H), 1.89−1.84 (m, 8H), 1.67 (s, 12H), 1.34−1.25 (m, 104H), 0.87 (t, ^3J = 6.9 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.82, 140.78, 140.5, 130.8, 130.7, 130.6, 130.0, 125.3, 125.2, 124.3, 122.5, 122.4, 122.3, 113.6, 112.84, 112.83, 112.5, 109.24, 109.16, 109.0, 92.3, 83.2, 82.7, 82.6, 82.5, 73.3, 73.1, 65.9, 43.4, 32.1, 31.8, 29.83, 29.81, 29.75, 29.69, 29.62, 29.51, 29.48, 29.0, 27.4, 22.8, 14.3. FT-IR (KBr): ν 3341 (br) (H−O-), 3057, 2925, 2853, 2213 (C≡C), 2139 (C≡C), 1626, 1596, 1482, 1381, 1352, 1286, 1234, 1133, 882, 806, 725 cm^{-1}. MALDI-TOF MS: *m*/*z* 1867.1 [M^+]. Anal. Calcd for $C_{134}H_{170}N_4O_2$: C, 86.12; H, 9.17; N, 3.00. Found: C, 85.78; H, 9.13; N, 2.99.

1,4-Bis{6-[(6-ethynyl-9-hexadecylcarbazol-3-yl)buta-1,3-diynyl]-9-hexadecylcarbazol-3-yl}buta-1,3-diyne (14). KOH (0.01 g, 0.18 mmol) was added to a stirred solution of **13** (0.081 g, 0.043 mmol) in methanol (0.5 mL) and toluene (5 mL). The mixture was refluxed for 4.5 h, and then it was diluted with dichloromethane and water. The phases were separated. The organic phase was dried over $MgSO_4$ and filtered. The filtrate was concentrated and purified by column chromatography on silica gel (dichloromethane/petroleum ether 1:2) to give **14** (0.071 g, 94%) as a light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.29−8.23 (m, 8H), 7.69−7.60 (m, 8H), 7.38−7.33 (m, 8H), 4.31−4.26 (m, 8H), 3.08 (s, 2H), 1.89−1.86 (m, 8H), 1.36−1.25 (m, 104H), 0.88 (t, ^3J = 6.9 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.8, 140.7, 130.74, 130.68, 130.3, 125.3, 124.9, 122.5, 122.4, 122.3, 113.0, 112.9, 112.8, 112.7, 109.2, 109.1, 84.9, 82.63, 82.61, 82.57, 75.7, 73.4, 73.3, 73.2, 43.5, 32.1, 29.9, 29.84, 29.77, 29.72, 29.6, 29.54, 29.50, 29.1, 27.4, 22.9, 14.3. FT-IR (KBr): ν 3056, 2960, 2924, 2853, 2210 (C≡C), 2140 (C≡C), 2105 (C≡C), 1626, 1596, 1480, 1381, 1352, 1261, 879, 803 cm^{-1}. MALDI-TOF MS: *m*/*z* 1751.4 [M^+]. Anal. Calcd for $C_{128}H_{158}N_4$: C, 87.72; H, 9.09; N, 3.20. Found: C, 87.67; H, 9.12; N, 3.21.

Synthesis of Macrocycle 2b by Intramolecular Cyclization. A solution of **14** (0.02 g, 0.011 mmol) in pyridine (11 mL) was added slowly to a mixture of CuCl (0.076 g, 0.77 mmol) and $CuCl_2$ (0.015 g, 0.11 mmol) in pyridine (44 mL) at room temperature. Upon completion of the slow addition (44 h), the reaction mixture was stirred for an additional 72 h. After removal of the solvent, the residual material was diluted with water, neutralized by dilute HCl solution, extracted with dichloromethane, washed with water, and dried over $MgSO_4$. The crude material was purified by TLC (petroleum ether/dichloromethane 1:1) to afford **2b** as a yellow solid (0.001 g, 10%). MALDI-TOF MS: *m*/*z* 1750.6 [M^+].

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Supporting Information Available: General experimental methods; NMR spectra of **1b**, **2b**, and **3a**−**14**; cyclic voltammetry curves of **14**, **1b**, and **2b**; and HRMS spectra of **4a**, **4b**, **5b**, and **6a**−**12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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