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Synthesis of Diverse *N*,*O*-Bridged Calix[1]arene[4]pyridine-C_{60} Dyads and Triads and Formation of Intramolecular Self-Inclusion Complexes

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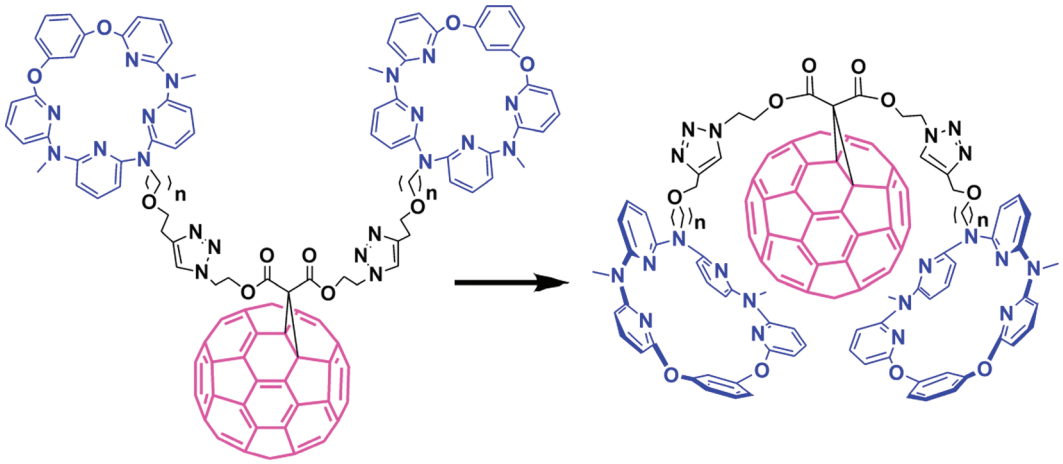

Starting from both the bridging nitrogen atom-functionalized and the upper rim-functionalized *N*,*O*-bridged calix[1]arene[4]pyridine reactants, different types of heteracalixaromatics-C_{60} dyads and triads of varied spacers were expediently synthesized using mainly the click reaction as the key step. By means of various spectroscopic methods, the heteracalixaromatics-C_{60} dyads and triads obtained have been shown to form intramolecular self-inclusion complexes rather than oligomers or polymers in solution because of a flexible spacer in between the heteracalixaromatic ring and C_{60} moiety. The current study, coupled with previous investigations, would provide the guideline for the construction of supramolecular fullerene motifs based on molecular design of the dyads and triads.

Introduction

Recent years have witnessed an increasing interest in fullerene chemistry.[1] Along with the very rapid and enormous development of functionalizations of fullerenes via the formation of various covalent bonds,[2] supramolecular fullerene chemistry or the nonchemical bonding interactions between fullerenes and synthetic host molecules has also attracted considerable attention. Based on a concave−convex interaction, for example, a few macrocyclic fullerene receptors such as azacrown ethers,[3] calixarenes,[4] cyclotriveratrilenes (CTV),[5] triptycenes,[6] cyclodextrins (CD),[7] and carbon nanorings[8]

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have been investigated. Porphyrins and metalloporphyrins with planar π-surfaces are also found to form complexes with fullerenes.[9] Bis-macrocyclic molecules, such as bisporphyrins ("Jaws")[10] and biscalixarenes,[11] have been explored to enhance the power of complexation with fullerenes. It is noteworthy that fullerene-based supramolecular oligomers and polymers, potentially useful optoelectronic materials, though very few, have been constructed by means of host−guest interactions. For example, Liu and co-workers have reported the first example of a water-soluble fullerene assembly between fullerenes and rigidified dimeric cyclodextrins.[12] The complementary molecular interaction between C_{60} and calix[5]arenes has been applied as a driving force for the preparation of a self-assembly network.[11c] Li and co-workers reported molecular assembly of zinc porphyrin-based molecular tweezers with fullerenes and derivatives.[13]

As a new generation of macrocyclic host molecules, heteracalixaromatics have recently received fast growing interest.[14−18] Because of the different electronic nature of heteroatoms compared with those of carbon, the heteroatom bridged calix(hetero)aromatics exhibit interesting structural and molecular recognition properties in contrast to conventional calixarenes. The bridging nitrogen atoms, for example, can adopt sp^2 and sp^3 electronic configurations and can form different degrees of conjugation with the adjacent aromatic rings, leading to the formation of versatile and fine-tuned macrocyclic structures and cavities.[14a,15d] Furthermore, various electronic effects of the heteroatoms can also influence the electron density of aromatic rings to yield the cavity of varied electronic features, and they exhibit versatile abilities to recognize different guests.[15d−f,l−q,16a,16k,16o−16q]

While macrocycles of a small cavity such as azacalix[4]pyridine do not interact with fullerene C_{60}, azacalix[*n*]pyridines (n = 5−10) and azacalix[4]arene[4]pyridine are powerful host molecules to complex with fullerenes C_{60} and C_{70} in solution. Very recently, we reported that *N*,*O*-bridged calix[1]arene[4]pyridines, unusual heteracalixaromatics bearing an odd number of different aromatic rings, form a 1:1 complex with fullerene C_{60} giving a binding constant ($K_{a(1:1)}$) of up to 49,494 M^{-1}.[18f] The easy preparation and functionalization of *N*,*O*-bridged calix[1]arene[4]pyridines both on the upper rim position (aromatic ring) and on the bridging nitrogen atom render these novel macrocylcles a unique platform for the construction of sophisticated molecular architectures. Our interest in the supramolecular fullerene chemistry, particularly in the construction of heteracalixaromatics−C_{60} complexes at both small molecular and oligomeric or polymeric levels, led us to undertake the present work. Herein we report the expedient synthesis of *N*,*O*-bridged calix[1]arene[4]pyridine−C_{60} dyads and triads containing different spacers mainly using click reaction as a key step. Interestingly, the resulting novel heteracalixaromatics−C_{60} dyads and triads all form self-inclusion complexes rather than the "head-to-tail" supramolecular oligomers and polymers because of the soft and flexible spacers.

Results and Discussion

Having functionalized *N*,*O*-bridged calix[1]arene[4]pyridines in hand,[18f] we decided to employ the click reaction strategy to

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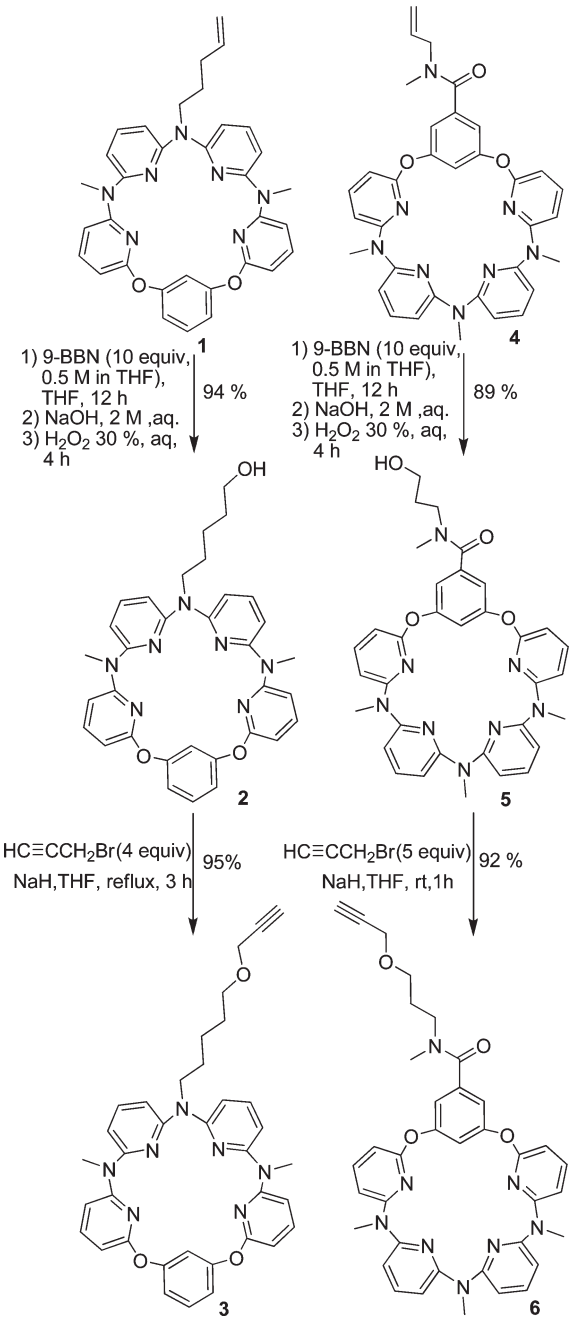
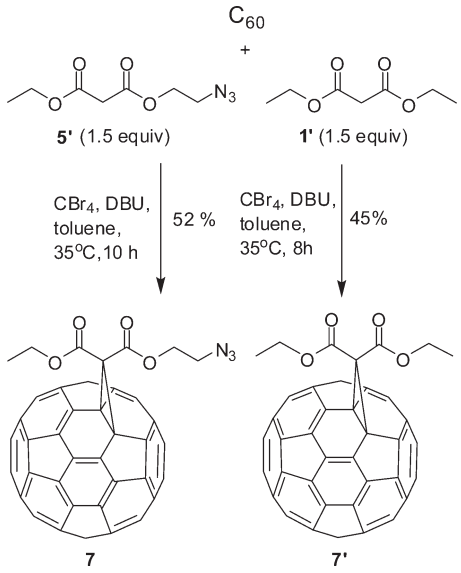
SCHEME 1. Synthesis of 3 and 6



construct heteracalixaromatics−C_{60} dyads and triads. Scheme 1 illustrates the synthesis of the acetylene components. The alkene group on the bridging nitrogen atom of macrocycle **1** was converted to primary alcohol **2** in an excellent yield after hydroboration and oxidation. In the presence of NaH, nucleophilic substitution reaction of **2** with propargyl bromide afforded a terminal alkyne product **3** almost quantitatively. Following the same procedures, acetylene compound **6** was prepared equally efficiently from **4** (Scheme 1).

By means of Bingel reaction[19] between C_{60} and diethyl malonate and azido-containing malonate (see Supporting Information, Scheme S1), the C_{60} derivatives **7** and **7′** were prepared (Scheme 2). The CuI-catalyzed 1,3-dipolar cycloaddition reaction of alkynes **3** and **6** with azide **7** produced the desired *N*,*O*-bridged calix[1]arene[4] pyridine−C_{60} dyads **8** and **9** in 98% and 97% yield, respectively (Scheme 3).

SCHEME 2. Synthesis of C_{60} derivatives 7 and 7′



Encouraged by the efficient synthesis of **8** and **9**, we then attempted the preparation of *N*,*O*-bridged calix[1]arene-[4]pyridine−C_{60} triads. The diazide compound **10** was first obtained from the Bingel reaction between C_{60} and 2-azidoethyl malonate (see Supporting Information, Scheme S2). The subsequent click reaction of the Bingel adduct **10** with 2 equiv of alkyne **3** led to the almost quantitative formation of *N*,*O*-bridged calix[1]arene[4]pyridine−C_{60} triad **11** (Scheme 4).

Since the length of a linker between heteracalixaromatics and C_{60} moiety may influence the host−guest interactions, we then synthesized a calix[1]arene[4]pyridine−C_{60} triad molecule using a shorter spacer. The ester of *N*,*O*-bridged calix-[1]arene[4]pyridine compound **12**, which was synthesized following a literature method,[18f] was reduced with $LiAlH_4$ to give a hydroxy compound **13** in 90%. Esterification of **13** upon treatment with malonate dichloride in the presence of Cs_2CO_3 as an acid scavenge furnished the biscalix[1]arene-[4]pyridine **14′** in 59% yield. Through the Bingel reaction between **14′** and C_{60} with DBU as a base, the *N*,*O*-bridged calix[1]arene[4]pyridine−C_{60} triad **14** bearing a shorter linker was obtained in 42% yield (Scheme 5). It should be noted that both the dyad molecule **8** and triad molecule **11** contain a linker between the bridging nitrogen of the calixarene and C_{60}, whereas in the case of dyad molecule **9** and triad molecule **14** the spacer is connected to the upper rim position of the benzene ring of the calixarene macrocycle.

For the purpose of comparison study, two *N*,*O*-bridged calix[1]arene[4] pyridine derivatives **8′** and **9′** and a biscalix-[1]arene[4]pyridine compound **11′**, which all contain no fullerene moiety, were also synthesized efficiently applying the same click reaction method (Scheme 6).

The structure of all products including the *N*,*O*-bridged calix[1]arene[4] pyridines **8′**, **9′**, **11′**, and **14′**, the corresponding heteracalixaromatics−C_{60} dyads **8** and **9**, and triads **11** and **14** was established on the basis of their spectroscopic

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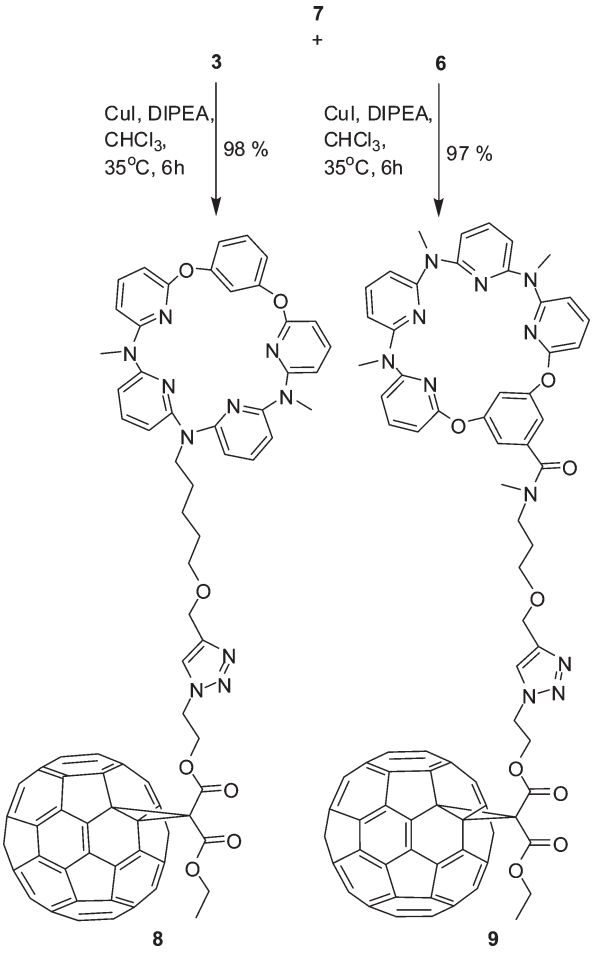
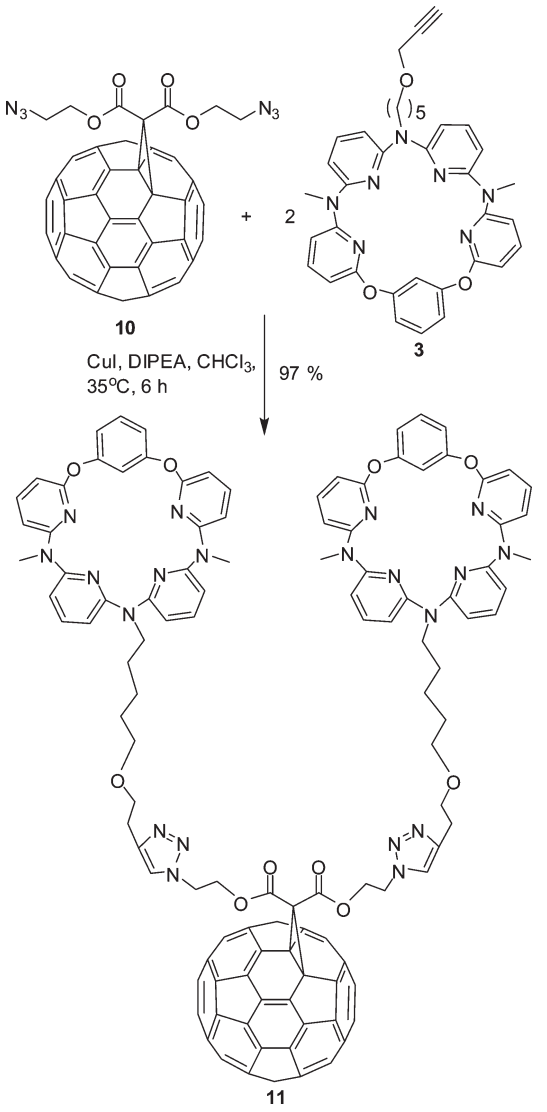
SCHEME 3. Synthesis of *N,O*-Bridged Calix[1]arene[4]pyridine–C_{60} Dyads 8 and 9



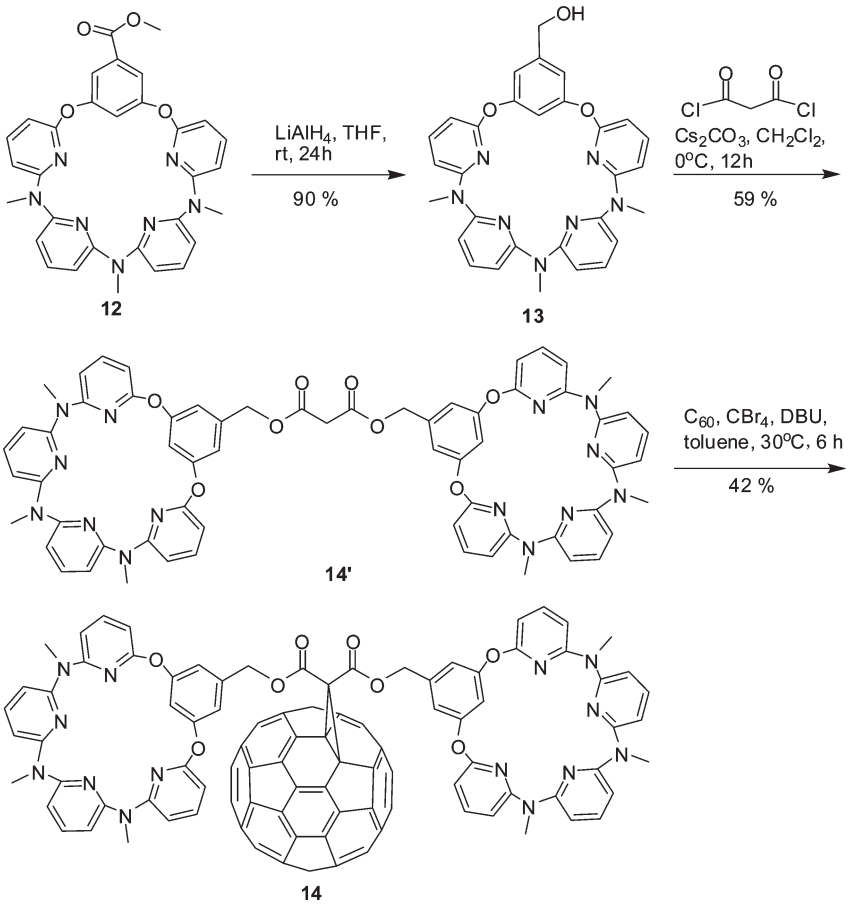
SCHEME 4. Synthesis of *N,O*-Bridged Calix[1]arene[4]pyridine–C_{60} Triad 11



data and microanalysis (see Supporting Information, Figures S16–S45). The assignment of proton signals in ^{1}H NMR was made by means of ^{1}H–^{1}H COSY NMR technique (see Supporting Information, Figure S1). As illustrated in Figure 1, introduction of a C_{60} moiety into heteracalixaromatic derivatives leads the proton signals H_a' (4.62 ppm), H_b' (8.05 ppm), H_c' (4.46 ppm), H_d' (4.05 ppm), and H_e' (1.13 ppm) in compound **8′** to shift downfield to H_a (4.94 ppm), H_b (8.11 ppm), H_c (4.84 ppm), H_d (4.45 ppm), and H_e (1.31 ppm), respectively, in heteracalixaromatics–C_{60} dyad **8**. The greater downfield shift of the proton signals H_a' (4.58 ppm), H_b' (8.04 ppm,) and H_c' (4.43 ppm) in compound **11′** to H_a (4.98 ppm), H_b (8.09 ppm), and H_c (4.86 ppm) in heteracalixaromatics–C_{60} triad **11** was also observed (Figure 1). Similar results were also found in the case of heteracalixaromatics–C_{60} dyad **9** and triad **14** when their ^{1}H NMR spectra were compared with that of *N,O*-bridged calix[1]arene[4] pyridines **9′** and **14′** (see Supporting Information, Figures S2 and S3). The downfield shift of the proton signals of dyads and triads indicates the deshielding effect of C_{60} moiety imposed on alkoxy protons, implying the proximity of these substituents to the C_{60} surface and therefore the self-inclusion of C_{60} moiety by heteracalixarenes ring(s) (*infra vide*).

As a prelude to the investigation of the molecular interaction of heteracalixaromatics–C_{60} dyads and triads synthesized, we initially studied the interaction of compounds **8′**, **9′**, **11′**, and **14′** with fullerene C_{60} and its Bingel adduct with diethyl malonate **7′**. As illustrated in Figure 3 and Figures S4–S5 in Supporting Information, the interaction of heteracalixarenes derivatives with C_{60} leads to a marginal blue shift of the maximum absorption (λ_{max}) of **7′** at about 488 nm in UV–vis absorption spectra. The titration of macrocyclic compounds with C_{60}, however, gave rise to the gradual quench of fluorescence intensity (Figure 2 and Figures S6–S10 in Supporting Information). Based on the Job's plot experiments (see inset in Figure 2 and Figures S6–S10 in Supporting Information), which gave the stoichiometry of the complex, and the fluorescence titration data, all *N,O*-bridged calix[1]arene[4]pyridine host molecules formed a 1:1 complex with fullerene C_{60} with a binding constant in the range of 34719 ± 1051 to 42041 ± 1321 M^{-1} (Table 1). It is worth noting that the binding ability of macrocyclic compounds **8′**, **9′**, **11′**, and **14′** toward C_{60} is comparable with that of the parent *N,O*-bridged calix[1]arene[4]pyridines,[18f] demonstrating that the substituent or a long "tail" attached either on the bridging nitrogen atom or on the upper-rim position of the benzene ring did not very

SCHEME 5. Synthesis of *N*,*O*-Bridged Calix[1]arene[4]pyridine-C60 Triad 14



much affect the interaction of macrocyclic ring with C_{60}. It is important to address that *N*,*O*-bridged calix[1]arene[4]pyridine derivatives **8′** and **11′** complexed equally well with the Bingel adduct of C_{60} with diethyl malonate **7′** under the identical conditions. The binding constants for 1:1 complexes of **8′·7′**, **11′·7′**, and **14′·7′** were 51224 ± 1441, 54979 ± 1625, and 51224 ± 1441 M^{-1}, respectively (Table 1).

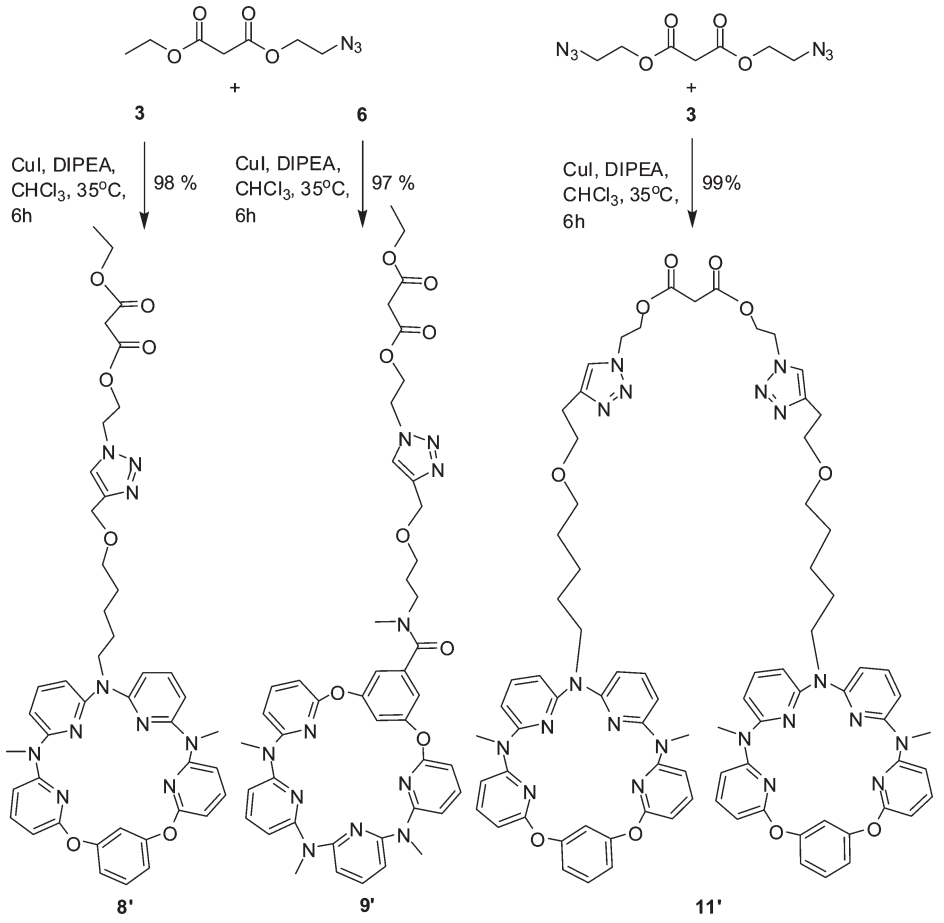
After revealing the strong complexation of *N*,*O*-bridged calix[1]arene[4]pyridine derivatives and bis-calix[1]arene-[4]pyridine with C_{60} and the Bingel adduct **7′**, we then examined the interaction of *N*,*O*-bridged calix[1]arene[4]pyridine−C_{60} dyads and triads. Figure 3 and Figures S4−S5 show the UV−vis spectra of *N*,*O*-bridged calix[1]arene[4]pyridine−C_{60} dyads and triads. The electronic absorption spectrum of a mixture of *N*,*O*-bridged calix[1]arene[4]pyridine compounds **8′**, **9′**, **11′**, and **14′** and the Bingel adduct of C_{60} were also depicted. The absorption of the Bingel adduct of C_{60} at 494 nm shifted hypsochromically to 488, 490, 488, and 487 nm when an equimolar amount of *N*,*O*-bridged calix-[1]arene[4]pyridine derivatives **8′**, **9′**, **11′**, and **14′** was added, respectively. A further hypsochromic shift was observed at 478, 486, 483, and 485 nm when C_{60} and macrocyclic ring was covalently bonded to form dyads and triads **8**, **9**, **11**, and **14**, respectively. A weak absorption band in a longer wavelength region (ca. 690 nm) gave the similar hypsochromic shift when the Bingel adduct was complexed and bonded with a macrocyclic ring (Figure 3 and Figure S4 in Supporting Information).

The interaction between macrocyclic ring and fullerene C_{60} moiety was clearly evidenced by the fluorescence spectroscopy. As shown in Figure 4, the parent macrocycles **8′** and **11′**, upon irradiation, gave a fluorescence emission band at 408 and 377 nm, respectively. In the presence of 1 equiv of C_{60}, the fluorescence intensity was quenched almost completely. Under the identical conditions, the dilute solution of dyad **8** and triad **11** did not emit at all, indicating a strong self-quenching effect between macrocycle and C_{60} moiety. Similar results of dyad **9** and triad **11** can also be observed in Figures S11−S12 in Supporting Information. The self-quenching of the fluorescence emission is most probably attributed to the *intramolecular* interaction between *N*,*O*-bridged calix[1]arene[4]pyridine concave and the convex of C_{60}, because the *intermolecular* interaction was easily excluded in a very dilute solution used. It is also important to note that the intramolecular quenching of fluorescence of heteracalixaromatics by the C_{60} group was most likely via a "space-to-space" mechanism since the flexible spacers did not favor a "through chemical bond" mechanism.[20]

To shed further light on the interaction of heterocalixacromatics−C_{60} dyads and triads, a number of other techniques were employed. The ^{1}H NMR spectra of the dyads and triads either in different concentrations (0.3−20 mM for **11** and 0.3−10 mM for **14**, respectively) (Figures S13−S14 in

(20) Tung, C.-H.; Zhang, L.-P.; Li, Y.; Cao, H.; Tanimoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 5348 and references therein.

SCHEME 6. Synthesis of *N*,*O*-Bridged Calix[1]arene[4]pyridine Derivatives 8′, 9′, and 11′



Supporting Information) and at varied temperatures (298−218 K) (Figure S15 in Supporting Information) did not show noticeable shift of the proton signals. These observations were in agreement with the formation of an intramolecular complex rather than the intermolecular "head-to-tail" oligomers or polymers. The very slight broadening of the proton signals at a low temperature was most probably due to the decrease of the flexibility of the macrocycle structure. Diffusion ^{1}H NMR (DOSY NMR) gave no evidence either for the intermolecular "head-to-tail" interactions between dyads or triads. Except for monomeric structures, no other peaks of larger molecular weights were observed from MALDI-TOF mass spectrometry (Figures S46−S49 in Supporting Information).

Taking all aforementioned results into consideration, both *N*,*O*-bridged calix[1]arene[4]pyridine−C_{60} dyads **8** and **9** and triads **11** and **14** formed the corresponding self-inclusion complexes rather than intermolecular "head-to-tail" aggregates. We proposed that, instead of forming the extended conformations such depicted in Schemes 3−5, the dyad and triad molecules adopt most likely the folded conformations (Figure 5). The structures of folded self-inclusion complexes of dyads and triads in Figure 5 were consistent with the observation of downfield shift of the alkoxy proton signals of dyads and triads (see Figure 1 and Figures S2−S3 in Supporting Information) (*supra vide*), as the alkoxy protons of dyads and triads are proximal to C_{60} moiety and experience the deshielding effect of the buckyball. The folded self-inclusion model may also best explain the complete quenching of fluorescence of heteracalixaromatics by C_{60} moiety through a space-to-space mechanism.[20]

As reported in the literature,[11c,12] the formation of supramolecular fullerene oligomers is achieved utilizing bis-cyclodextrin or bis-calix[5]arene with a very rigid linker. The dominant formation of intramolecular self-inclusion complexes of dyads and triads in the current study is most probably due to the molecular flexibility. With a soft and flexible spacer such as an alkylene chain in between host and guest moieties, intramolecular calixarene−C_{60} interaction wins over intermolecular interaction.

Conclusion

In summary, we have synthesized both the upper rim-linked and the bridging nitrogen-linked *N*,*O*-bridged calix[1]arene[4]pyridine−C_{60} dyads and triads using click reaction protocol from conveniently available functionalized heteracalixaromatics. By means of UV−vis and fluorescence spectroscopy, NMR techniques, and MALDI-TOF mass spectrometric methods, the novel dyads and triads prepared have been shown to form dominantly intramolecular self-inclusion complexes rather than intermolecular interacted oligomers or polymers. This is most probably because of a flexible spacer in between the heteracalixaromatics ring and C_{60} moiety. The use of a rigid linker in dyads and triads, which prohibits the folding of the molecular conformation, would enable the formation of "head-to-tail" supramolecular

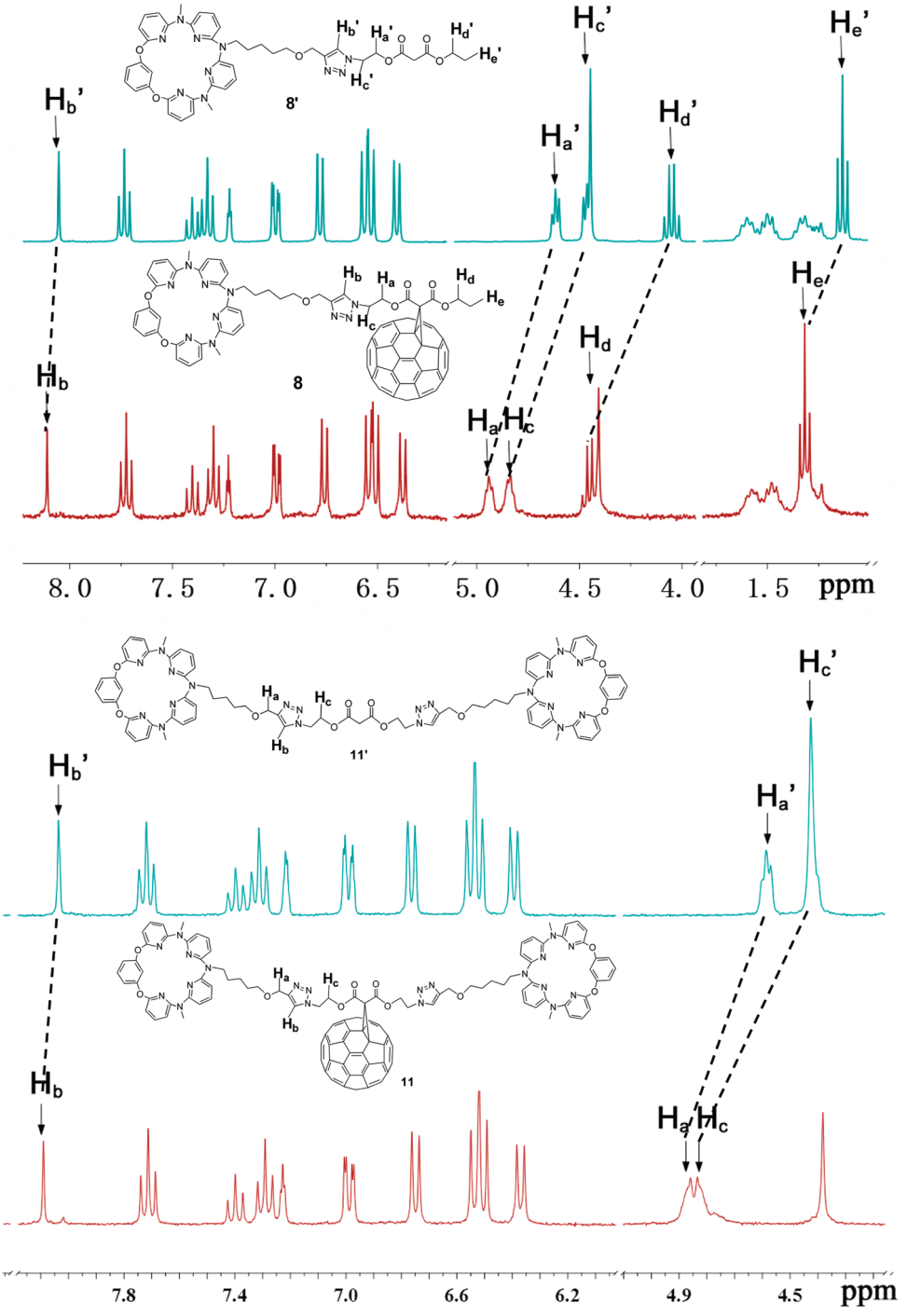


FIGURE 1. ^{1}H NMR spectrum of compounds **8′** and **8**, **11′** and **11**.

fullerene aggregates. The outcomes of the current study and of previous investigations would provide a useful guideline for the construction of supramolecular fullerene motifs based on molecular design of the dyads and triads.

Experimental Section

General Procedure for the Synthesis of *N*,*O*-Bridged Calix[1]arene[4]pyridine Derivatives 2 and 5. 9-BBN (15 mmol in 30 mL THF) was added to a solution of **1** (836 mg, 1.5 mmol) or **4** (900 mg, 1.5 mmol) in dry THF (200 mL) under argon protection. The mixture was reacted for 12 h in an ice-bath followed by the addition of NaOH (2M, 11 mL). Then H_2O_2 (30%, 17 mL) was added into the mixture for 1 h. The resulting mixture was kept for 4 h in an ice-bath and another 4 h at room temperature. Brine (200 mL) was added to the mixture, and the aqueous phase was extracted with CH_2Cl_2 twice (200 mL × 2). The organic phase was washed with NaOH (2 M) solution three times and then dried with anhydrous Na_2SO_4. After filtration and removal of the solvent, the residue was chromatographed on a silica gel column with a 1:1 mixture of petroleum ether and ethyl acetate as the mobile phase to give pure **2** (813 mg, 94%) or **5** (823 mg, 89%) as a pale yellow solid. **Data for 2**: mp 61−62 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (t, J_1 = 4.5 Hz, J_2 = 7.9 Hz, 2H), 7.47 (b, 1H), 7.39 (t, J_1 = 8.0 Hz, J_2 = 8.0 Hz, 2H),

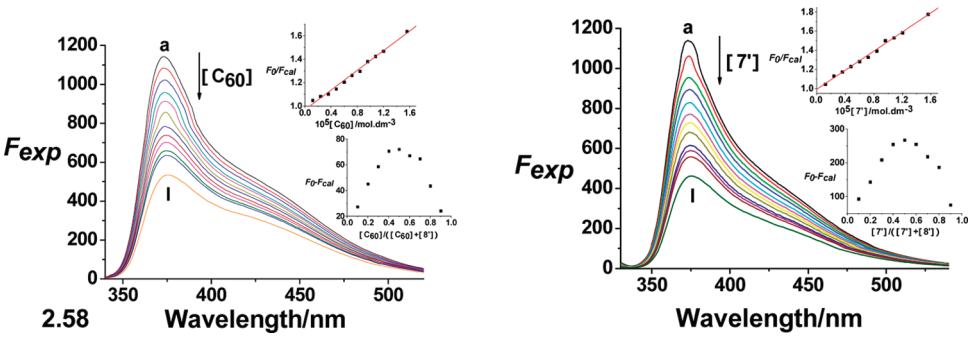


FIGURE 2. Emission spectra (λ_{ex} = 321 nm) of **8′** (3.2×10^{-5} M) in the presence of C_{60} (left) and **7′** (right) in toluene at 25 °C. The concentrations of C_{60} for curves a−l (from top to bottom) are 0, 1.20, 2.40, 3.60, 4.80, 6.00, 7.20, 8.40, 9.60, 10.80, 12.00, and 15.60 ($\times 10^{-6}$ M). The concentrations of **7′** for curves a−l (from top to bottom) are 0, 1.20, 2.40, 3.60, 4.80, 6.00, 7.20, 8.40, 9.60, 10.80, 12.00, and 15.60 ($\times 10^{-6}$ M). Insets: The up insets are the variation of fluorescence intensity F_0/F_{cal} of **8′** with increasing C_{60} concentration (left) and with increasing **7′** concentration (right). The down insets are the Job plots for **8′**·C_{60} (left) and **8′**·**7′** (right) complex in toluene solution (total concentration is 2.4×10^{-5} M).

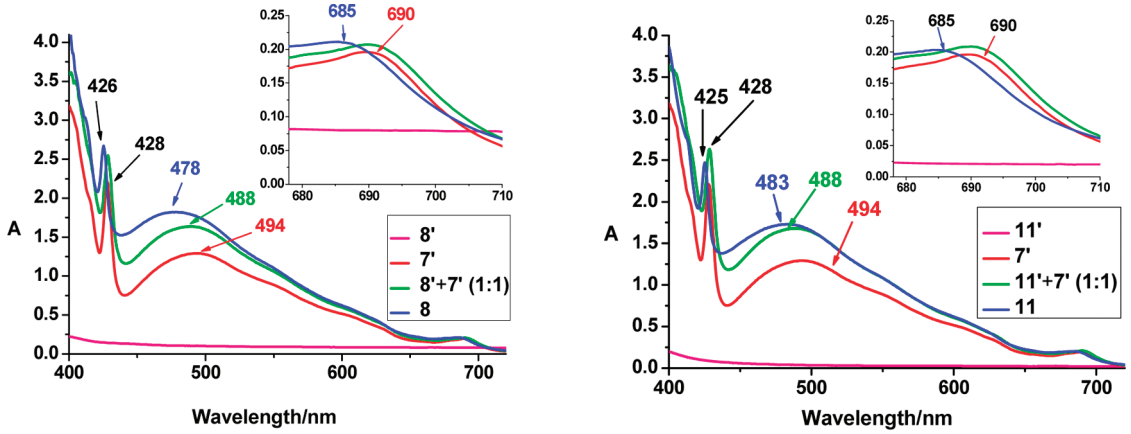


FIGURE 3. Absorption spectra of *N*,*O*-bridged calix[1]arene[4]pyridine derivatives **8′** and **11′**, C_{60} derivative **7′**, 1:1 mixture of **8′** and **7′**, **11′** and **7**, and *N*,*O*-bridged calix[1]arene[4]pyridine−C_{60} dyad **8** and triad **11**. The concentration for all compounds is 1.0×10^{-3} M.

TABLE 1. Association Constants for the 1:1 Complexation of *N*,*O*-Bridged Calix[1]arene[4]pyridines with Fullerene C_{60} and Bingel Adduct 7′[a]

compound	K_α (1:1 complexation with C_{60}) (M^{-1})	K_α (1:1 complexation with **7′**) (M^{-1})
8′	42041 ± 1321	49992 ± 1321
9′	34719 ± 1051	*b*
11′	37177 ± 1097	54979 ± 1625
14′	40978 ± 1330	51224 ± 1441

[a]The association constants were calculated using a Stern−Volmer equation based on fluorescence titration data. [b]Not determined.

7.34 (t, J = 8.2 Hz, 1H), 6.96 (dd, J_1 = 8.1 Hz, J_2 = 2.2 Hz, 2H), 6.61−6.56 (m, 6H), 6.38 (d, J = 8.0 Hz, 2H), 3.91 (t, J = 7.4 Hz, 2H), 3.61 (t, J = 6.4 Hz, 2H), 3.39 (s, 6H), 1.72 (quintet, J = 7.5 Hz, 2H), 1.59 (quintet, J = 7.5 Hz, 2H), 1.72 (quintet, J = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.3, 156.9, 155.9, 155.6, 154.6, 140.5, 138.3, 129.5, 114.5, 114.4, 108.5, 107.9, 106.6, 103.4, 62.8, 48.7, 36.7, 32.5, 28.2, 23.4; IR (KBr) 3331, 2928, 1590, 1573 cm^{-1}; MS (MALDI-TOF) m/z 576.2 $[M + H]^+$, 598.2 $[M + Na]^+$, 614.2 $[M + K]^+$. Anal. Calcd for $C_{33}H_{33}N_7O_3$ $[M + H]^+$: 575.2645. Found: 575.2649 $[M + H]^+$. **Data for 5**: mp 69−70 °C; ^{1}H NMR (300 MHz, CD_3OD) δ 7.74 (t, J = 7.9 Hz, 2H), 7.53−7.64 (br, 1H), 7.41 (t, J = 8.0 Hz, 2H), 7.00−7.10 (br, 2H), 6.79 (d, J = 8.0 Hz), 6.55−6.68 (m, 4H), 6.58 (d, J = 7.9 Hz, 2H), 3.57−3.72 (m, 2H), 3.40 (s, 9H), 2.97−3.12 (m, 3H), 1.68−1.97 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.0, 170.6, 160.9, 156.9, 156.0, 155.5, 154.2, 140.8, 138.2, 137.2, 115.6, 15.4, 108.8, 107.5, 106.5, 103.9, 103.6, 58.9, 58.3, 48.4, 44.0, 37.4, 36.8, 35.8, 32.9, 30.9, 29.3; IR (KBr) 3397, 1635, 1617, 1590, 1568 cm^{-1}; MS (MALDI-TOF) m/z:619.4 $[M + H]^+$, 641.4 $[M + Na]^+$, 657.4 $[M + K]^+$. Anal. Calcd for $C_{34}H_{34}N_8O_4$ $[M + H]^+$: 618.2703. Found: 618.2708 $[M + H]^+$.

Synthesis of *N*,*O*-Bridged Calix[1]arene[4]pyridine Derivative 3. NaH (1440 mg, 60 mmol), **2** (863 mg, 1.5 mmol), and 3-bromoprop-1-yne (714 mg, 6 mmol) were dissolved in dried THF. The mixture was stirred for 1 h at room temperature and then refluxed for 3 h. The mixture was cooled in an ice-bath, and ammonium chloride (10 mL) was added slowly. After removal of solvent, water (100 mL) was added, and the mixture was extracted with CH_2Cl_2 three times (100 mL × 3). The organic phase was dried with anhydrous Na_2SO_4. After filtration and removal of the solvent, the residue was chromatographed on a silica gel column with a mixture of petroleum ether and ethyl acetate as the mobile phase to give pure **3** (876 mg, 95%) as a pale yellow solid: mp 54−55 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (t, J_1 = 8.0 Hz, J_2 = 7.8 Hz, 2H), 7.49 (t, J = 2.4 Hz, 1H), 7.36 (t, J_1 = 7.9 Hz, J_2 = 7.9 Hz, 2H), 7.34 (t, J = 7.9 Hz, 1H), 6.96 (dd, J_1 = 8.1 Hz, J_2 = 2.2 Hz, 2H), 6.60−6.52 (m, 6H), 6.36 (d, J = 8.0 Hz, 2H), 4.10 (d, J = 2.4 Hz, 2H), 3.88 (t, J = 7.5 Hz, 2H), 3.49 (t, J = 6.5 Hz, 2H), 3.38 (s, 6H), 2.39 (t, J = 2.3 Hz, 1H), 1.71 (quintet, J = 7.5 Hz, 2H), 1.62 (quintet, J = 7.5 Hz, 2H), 1.41 (quintet, J = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.4, 157.1, 156.0, 155.7, 154.7, 140.5, 138.2, 129.5, 116.6, 114.4, 108.6, 108.0, 106.5, 103.4, 80.1, 74.0, 70.1, 58.0, 48.8, 29.4, 28.3, 23.9; IR (KBr) 3291, 2113, 1590, 1564 cm^{-1}; MS (MALDI-TOF) m/z 614.4 $[M + H]^+$, 636.4 $[M + Na]^+$, 652.4 $[M + K]^+$. Anal. Calcd for $C_{36}H_{35}N_7O_3$: C, 70.45; H, 5.75; N, 15.98. Found: C, 70.73; H, 6.02; N, 15.87.

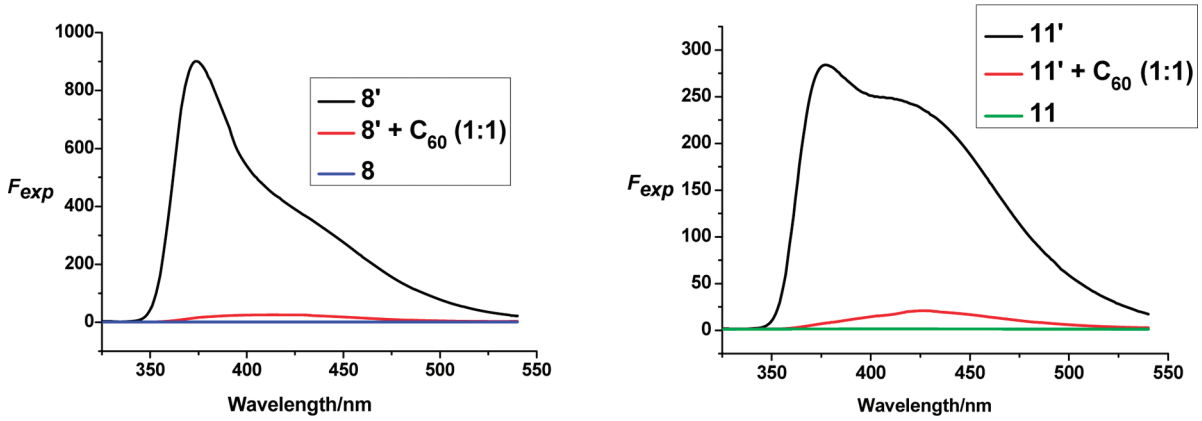


FIGURE 4. Fluorescence spectra of *N*,*O*-bridged calix[1]arene[4]pyridine derivatives **8′** (1.0×10^{-4} M) and **11′** (1.0×10^{-4} M), and of the 1:1 mixture of **8′** and C_{60}, **11′** and C_{60}, and of the *N*,*O*-bridged calix[1]arene[4]pyridine−C_{60} dyad **8** (1.0×10^{-4} M) and triad **11** (1.0×10^{-4} M).

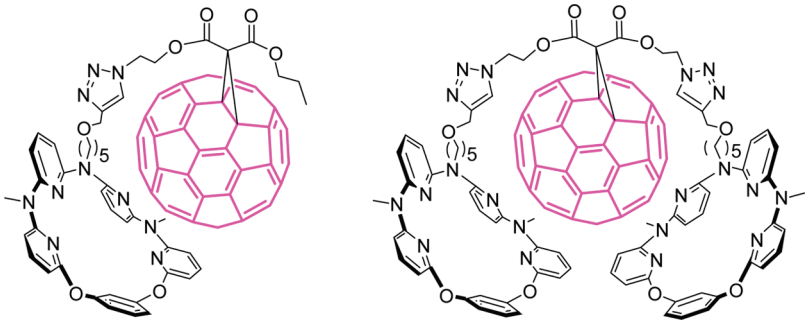


FIGURE 5. Schematic illustration of the intramolecular self-inclusion of the *N*,*O*-bridged calix[1]arene[4]pyridine−C_{60} dyad **8** and triad **11** molecules.

Synthesis of *N*,*O*-Bridged Calix[1]arene[4]pyridine Derivative 6. NaH (240 mg, 10 mmol), **5** (618 mg, 1 mmol), and 3-bromoprop-1-yne (595 mg, 5 mmol) were dissolved in dried THF. The mixture was stirred for 1 h at room temperature and then refluxed for 3 h. The mixture was cooled in an ice-bath, and ammonium chloride (10 mL) was added slowly. After removal of solvent, water (100 mL) was added, and the mixture was extracted with CH_2Cl_2 three times (100 mL × 3). The organic phase was dried with anhydrous Na_2SO_4. After filtration and removal of the solvent, the residue was chromatographed on a silica gel column with a mixture of petroleum ether and ethyl acetate as the mobile phase to give pure **6** (604 mg, 92%) as a pale yellow solid: mp 75−76 °C; ^{1}H NMR (300 MHz, d_6-acetone) δ 7.75 (t, J = 7.9 Hz, 2H), 7.40 (t, J = 8.0 Hz, 2H), 7.34 (s, 1H), 7.03 (s, 2H), 6.82 (d, J = 7.9 Hz, 2H), 6.62 (d, J = 8.0 Hz, 2H), 6.51−6.60 (m, 4H), 3.89−4.30 (m, 2H), 3.48−3.69 (br, 2H), 3.21−3.47 (m, 11H), 2.84−3.06 (m, 4H), 1.67−1.98 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6, 160.9, 156.9, 156.1, 155.4, 154.3, 140.7, 138.3, 138.1, 115.4, 115.3, 115.0, 108.7, 107.6, 106.6, 103.5, 79.7, 74.5, 67.7, 66.7, 58.1, 48.6, 45.2, 37.9, 36.8, 35.9, 33.0, 28.4, 27.1; IR (KBr) 3291, 3225, 2113, 1630, 1590, 1568 cm^{-1}; MS (MALDI-TOF) m/z 657.4 $[M + H]^+$, 679.4 $[M + Na]^+$, 695.4 $[M + K]^+$. Anal. Calcd for $C_{37}H_{36}N_8O_4$: C, 67.67; H, 5.53; N, 17.06. Found: C, 67.62; H, 5.65; N, 17.22.

Synthesis of *N*,*O*-Bridged Calix[1]arene[4]pyridine Derivative 8′. Diisopropylethylamine (5 mL) and CuI (153 mg, 0.8 mmol) were added to a solution of **3** (245 mg, 0.4 mmol) and 2-azidoethyl ethyl malonate (161 mg, 0.8 mmol) in $CHCl_3$ (10 mL). The mixture was stirred for 2 h at room temperature. After filtration and removal of the solvent, the residue was chromatographed on a silica gel column with a mixture of petroleum ether and ethyl acetate as the mobile phase to give pure **8′** (320 mg, 98%) as pale yellow solid: mp 39−40 °C; ^{1}H NMR (300 MHz, d_6-DMSO) δ 8.05 (s, 1H), 7.73 (t, J = 7.9 Hz, 2H), 7.40 (t, J = 8.2 Hz, 1H), 7.33 (t, J = 8.0 Hz, 2H), 7.22 (t, J = 2.1 Hz, 1H), 7.99 (dd, J_1 = 8.2 Hz, J_2 = 2.1 Hz, 2H), 6.78 (d, J = 8.0 Hz, 2H), 6.56 (d, J = 8.2 Hz, 2H), 6.53 (J = 8.0 Hz, 2H), 6.40 (d, J = 7.9 Hz, 2H), 4.61 (t, J = 4.7 Hz, 2H), 4.46 (t, J = 5.3 Hz, 2H), 4.46 (s, 2H), 4.05 (q, J = 7.1 Hz, 2H), 3.78 (t, J = 7.1 Hz, 2H), 3.46 (s, 2H), 3.38 (t, J = 6.5 Hz, 2H), 3.26 (s, 6H), 1.43−1.67 (m, 4H), 1.27−1.38 (m, 2H), 1.13 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1, 166.0, 161.2, 156.9, 155.8, 155.5, 154.5, 145.9, 140.6, 138.2, 129.5, 123.1, 116.5, 114.4, 108.4, 107.8, 106.5, 103.4, 70.6, 64.3, 63.3, 61.7, 48.8, 48.7, 41.2, 36.7, 29.4, 28.2, 23.8; IR (KBr) 2933, 1750, 1733, 1599, 1568 cm^{-1}; MS (MALDI-TOF) m/z 815.5 $[M + H]^+$, 837.5 $[M + Na]^+$, 853.6 $[M + K]^+$. Anal. Calcd for $C_{43}H_{46}N_{10}O_7$ $[M + H]^+$: 815.3624. Found: 815.3612 $[M + H]^+$.

Synthesis of *N*,*O*-Bridged Calix[1]arene[4]pyridine Derivative 9′. Diisopropylethylamine (5 mL) and CuI (86 mg, 0.4 mmol) were added to a solution of **6** (142 mg, 0.2 mmol) and 2-azidoethyl ethyl malonate (80 mg, 0.4 mmol) in $CHCl_3$ (10 mL). The mixture was stirred for 2 h at room temperature. After filtration and removal of the solvent, the residue was chromatographed on a silica gel column with a mixture of acetone and dichloromethane as the mobile phase to give pure **9′** (165 mg, 97%) as a pale yellow solid: mp 43−44 °C; ^{1}H NMR (300 MHz, CD_3OD) δ 7.66−7.92 (d, J = 27.0 Hz, 1H), 7.63 (t, J = 8.0 Hz, 2H), 7.39−7.51 (d, J = 18.7 Hz, 1H), 7.28 (t, J = 7.7 Hz, 2H), 6.89 (s, 2H), 6.67 (d, J = 7.8 Hz, 2H), 6.49 (t, J = 8.3 Hz, 4H), 6.40 (t, J = 7.5 Hz, 2H), 4.22−4.61 (m, 6H), 4.02 (m, 2H), 3.51 (t, J = 6.2 Hz, 2H), 3.25−3.45 (m, 13H), 2.79−2.96 (m, 3H), 1.63−1.90 (m, 2H), 1.10 (q, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.3, 169.9, 166.1, 165.9, 160.9, 156.9, 155.9, 155.4, 154.3, 145.1, 140.7, 138.1, 123.3, 115.2, 108.8, 107.4, 106.4, 103.5, 68.0, 67.4, 64.3,

63.3, 61.6, 48.7, 45.0, 41.2, 37.6, 36.7, 35.7, 32.8, 28.4, 27.2, 14.0; IR (KBr) 2923, 1750, 1732, 1626, 1595, 1568 cm^{-1}; MS (MALDI-TOF) *m/z* 858.6 $[M + H]^+$, 880.6 $[M + Na]^+$, 896.6 $[M + K]^+$. Anal. Calcd for $C_{44}H_{47}N_{11}O_8$ $[M + H]^+$: 858.3682. Found: 858.3693 $[M + H]^+$.

Synthesis of *N,O*-Bridged Calix[1]arene[4]pyridine Derivative 11′. Diisopropylethylamine (30 mL) and CuI (153 mg, 0.8 mmol) were added to a solution of **3** (245 mg, 0.4 mmol) and bis-(2-azidoethyl) malonate (48 mg, 0.2 mmol) in $CHCl_3$ (10 mL). The mixture was stirred for 2 h at room temperature. Then more bis(2-azidoethyl) malonate (24 mg, 0.1 mmol) was added, and the mixture was kept for another 1 h. After filtration and removal of the solvent, the residue was chromatographed on a silica gel column with a mixture of acetone and dichloromethane as the mobile phase to give pure **11′** (289 mg, 99%) as a pale yellow solid: mp 65−67 °C; ^{1}H NMR (300 MHz, d_6-DMSO) δ 8.04 (s, 2H), 7.72 (t, J = 7.9 Hz, 4H), 7.40 (t, J = 8.3 Hz, 2H), 7.31 (t, J = 8.1 Hz, 4H), 7.22 (t, J = 1.9 Hz, 2H), 7.69 (dd, J_1 = 8.3 Hz, J_2 = 1.9 Hz, 4H), 6.76 (d, J = 7.8 Hz, 4H), 6.55 (d, J = 8.1 Hz, 4H), 6.52 (d, J = 8.3 Hz, 4H), 6.39 (d, J = 8.0 Hz, 4H), 4.59 (t, J = 5.0 Hz, 4H), 4.43 (m, 8H), 3.76 (t, J = 7.0 Hz, 4H), 3.42−3.66 (m, 4H), 3.38 (m, 4H), 3.25 (s, 12H), 1.58 (m, 4H), 1.47 (m, 4H), 1.29 (m, 4H); ^{13}C NMR (75 MHz, d_6-DMSO) δ 165.8, 160.6, 156.6, 155.4, 154.7, 154.0, 144.2, 141.3, 138.4, 129.8, 124.0, 116.6, 113.1, 110.0, 107.2, 105.8, 104.3, 79.1, 71.9, 69.5, 63.2, 63.1, 48.2, 47.6, 36.4, 29.5, 28.8, 27.5, 23.2; IR (KBr) 2933, 1750, 1733, 1595, 1567 cm^{-1}; MS (MALDI-TOF) *m/z* 1469.8 $[M + H]^+$, 1491.8 $[M + Na]^+$, 1507.8 $[M + K]^+$. Anal. Calcd for $C_{79}H_{80}N_{20}O_{10}$ $[M + H]^+$: 1469.6439. Found: 1469.6469 $[M + H]^+$.

General Procedure for the Synthesis of N,O-Bridged Calix-[1]arene[4]pyridine−C_{60} Dyads 8 and 9. Under argon protection, a mixture of C_{60} (500 mg, 0.694 mmol) and dried toluene (500 mL) was stirred until the C_{60} was thoroughly dissolved. The flask was covered with kitchen foil to avoid light. A solution of 2-azidoethyl ethyl malonate (210 mg, 1.045 mmol) and a solution of CBr_4 (1152 mg, 3.470 mmol) in dried toluene were added consecutively. Then a solution of DBU (1055 mg, 6.940 mmol) in dried toluene (approximately 20 mL) was injected slowly to the mixture during 4 h. The resulting mixture was reacted for another 6 h. After completion of the reaction, water (500 mL) was added, and the organic phase was separated and dried with anhydrous Na_2SO_4. After filtration, the mixture was concentrated to approximately 30 mL (*Caution! The complete removal of the solvent caused decomposition of the product*). Column chromatography on a silica gel column eluted with first CS_2 to remove unconsumed C_{60} and then with a mixture of CS_2 and CH_2Cl_2 (1:1) to give a black solution. After concentrating to approximately 10 mL, $CHCl_3$ (130 mL) was added. To the resulting solution was added **3** (425 mg, 0.694 mmol) or **6** (455 mg, 0.694 mmol), CuI (1910 mg, 10 mmol), and diisopropylethylamine (50 mL). The mixture was kept at room temperature for 6 h. After filtration and removal of solvent, the residue was chromatographed on a silica gel column with a mixture of acetone, dichloromethane and carbon bisulfide (1:3:3) as the mobile phase to give pure **8** (524 mg, 51%) or **9** (546 mg, 50%) as a dark brown solid. **Data for 8**: mp 120−121 °C; ^{1}H NMR (300 MHz, d_6-DMSO) δ 8.11 (s, 1H), 7.73 (t, J = 7.9 Hz, 2H), 7.40 (t, J = 8.2 Hz, 1H), 7.30 (t, J = 7.9 Hz, 2H), 7.23 (s, 1H), 6.99 (dd, J_1 = 7.9 Hz, J_2 = 2.1 Hz, 2H), 6.76 (d, J = 7.9 Hz, 2H), 6.46−6.52 (m, 4H), 6.38 (d, J = 7.9 Hz, 2H), 4.94 (br, 2H), 4.83 (br, 2H), 4.45 (q, J = 6.9 Hz, 2H), 4.41 (s, 2H), 3.76 (t, J = 6.6 Hz, 2H), 3.37 (t, J = 6.4 Hz, 2H), 3.25 (s, 6H), 1.52−1.63 (m, 2H), 1.41−1.52 (m, 2H), 1.20−1.37 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2, 163.1, 161.2, 156.9, 155.7, 155.5, 154.5, 145.93, 145.26, 145.18, 145.00, 144.96, 144.92, 144.89, 144.82, 144.67, 144.64, 144.58, 144.49, 143.86, 143.82, 143.05, 143.02, 142.92, 142.16, 142.15, 141.82, 141.80, 140.97, 140.85, 140.59, 139.22, 138.64, 138.25, 129.5, 122.9, 116.6, 114.4, 108.5, 107.9, 106.5, 103.5, 71.2, 70.8, 54.9, 64.5, 63.7, 51.7, 48.8, 48.7, 36.8, 29.5, 28.2, 23.9, 14.3; IR (KBr) 1746, 1732, 1590, 1564 cm^{-1}; MS (MALDI-TOF) *m/z* 1534.4 $[M + H]^+$, 1556.3 $[M + Na]^+$, 1572.3 $[M + K]^+$. Anal. Calcd for $C_{103}H_{44}N_{10}O_7$ $[M + H]^+$: 1533.3467. Found: 1533.3465 $[M + H]^+$. **Data for 9**: mp 178−179 °C; ^{1}H NMR (300 MHz, d_6-DMSO, 380 K) δ 7.98 (s, 1H), 7.70 (t, J = 7.7 Hz, 2H), 7.35 (t, J = 7.6 Hz, 2H), 7.18−7.28 (br, 1H), 6.90 (d, J = 1.7 Hz, 2H), 6.78 (d, J = 7.7 Hz, 2H), 6.34−6.63 (m, 6H), 4.85−4.96 (br, 2H), 4.72−4.85 (br, 2H), 4.32−4.51 (m, 4H), 3.32−3.50 (m, 5H), 3.30 (s, 3H), 3.26 (s, 6H), 1.59−1.85 (m, 2H), 1.36 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 170.4, 163.2, 161.0, 156.9, 156.0, 155.4, 154.3, 145.59, 145.24, 145.16, 145.01, 144.96, 144.87, 144.65, 144.61, 144.58, 144.46, 143.85, 143.79, 143.62, 143.05, 143.00, 142.90, 142.65, 142.16, 142.14, 141.81, 140.91, 140.82, 139.18, 138.61, 138.25, 127.77, 123.2, 115.1, 114.0, 109.0, 108.7, 107.5, 106.6, 106.3, 103.6, 71.3, 68.3, 67.5, 64.8, 64.7, 63.7, 51.8, 48.7, 45.0, 37.8, 36.8, 35.8, 32.9, 28.6, 27.2, 14.2; IR (KBr) 1750, 1715, 1640, 1591, 1569 cm^{-1}; MS (MALDI-TOF) *m/z* 1577.5 $[M + H]^+$, 1599.5 $[M + Na]^+$, 1615.5 $[M + K]^+$. Anal. Calcd for $C_{104}H_{46}N_{11}O_8$ $[M + H]^+$: 1576.3525. Found: 1576.3512 $[M + H]^+$.

Synthesis of *N,O*-Bridged Calix[1]arene[4]pyridine−C_{60} Triad 11. Following the same procedure for the preparation of **8** or **9**, **11** (1053 mg, 49%) was obtained from the reaction of **3** (851 mg, 1.388 mmol) as a dark brown solid: mp 149−150 °C; ^{1}H NMR (300 MHz, d_6-DMSO) δ 8.09 (s, 2H), 7.71 (t, J = 8.0 Hz, 4H), 7.40 (t, J = 8.1 Hz, 2H), 7.29 (t, J = 7.9 Hz, 4H), 7.23 (t, J = 2.1 Hz, 2H), 6.98 (dd, J_1 = 8.0 Hz, J_2 = 2.1 Hz, 4H), 6.75 (d, J = 8.1 Hz, 4H), 6.53 (d, J = 8.0 Hz, 4H), 6.50 (d, J = 8.0 Hz, 4H), 6.37 (d, J = 8.0 Hz, 4H), 4.68−4.95 (m, 8H), 4.38 (s, 4H), 3.74 (t, J = 6.3 Hz, 4H), 3.24 (s, 12H), 1.50−1.62 (m, 4H), 1.39−1.49 (m, 4H), 1.31−1.32 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.6, 161.3, 156.9, 155.7, 155.5, 154.5, 145.79, 145.24, 145.17, 144.91, 144.83, 144.66, 144.61, 144.49, 144.45, 143.80, 143.00, 142.93, 412.12, 141.77, 140.94, 140.62, 138.84, 138.25, 129.5, 123.1, 116.6, 114.6, 108.6, 107.8, 106.5, 103.5, 70.9, 10.8, 65.0, 64.4, 60.4, 51.2, 48.7, 36.8, 29.4, 28.2, 23.9; IR (KBr) 1746, 1732, 1595, 1573 cm^{-1}; MS (MALDI-TOF) *m/z* 2188.3 $[M + H]^+$, 2210.3 $[M + Na]^+$, 2226 $[M + K]^+$. Anal. Calcd for $C_{139}H_{79}N_{20}O_{10}$ $[M + H]^+$: 2187.6283. Found: 2187.6253 $[M + H]^+$.

Synthesis of *N,O*-Bridged Calix[1]arene[4]pyridine Derivative 13. Under argon protection and at 0 °C, $LiAlH_4$ (2280 mg, 60 mmol) in THF (100 mL) was added slowly into a solution of **12** (1686 mg, 3 mmol) in dried THF (100 mL) for 2 h. It was reacted for another 4 h at 0 °C and then 18 h at room temperature. After completion of the reaction, the mixture was cooled down to 0 °C with an ice-bath, ethyl acetate (50 mL) was added for 1 h, and the mixture was stirred for 2 h. Then methanol (50 mL) was added for 1 h, and the mixture was reacted for 5 h at 0 °C and 2 h at room temperature. $CHCl_3$ (200 mL) was added for 1 h while stirring. After filtration, the filter residue was mixed with another 200 mL of $CHCl_3$ and was kept stirring for another 1 h followed by filtration. The filtrate was combined and dried with anhydrous Na_2SO_4. After removal of organic solvent, the residue was chromatographed on a silica gel column with a mixture of acetone and dichloromethane (1:3) as the mobile phase to give pure product **13** (1441 mg, 90%) as a white solid: mp 210−211 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (t, J = 7.9 Hz, 2H), 7.44 (t, J = 1.8 Hz, 1H), 7.40 (t, J = 8.0 Hz, 2H), 7.00 (d, J = 2.1 Hz, 2H), 6.63 (d, J = 7.9 Hz, 2H), 6.59 (d, J = 8.0 Hz, 4H), 6.40 (d, J = 8.0 Hz, 2H), 4.72 (s, 2H), 3.43 (s, 3H), 3.41 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.2, 156.9, 156.2, 155.4, 154.4, 143.2, 140.5, 138.1, 114.8, 113.5, 108.3, 107.5, 106.6, 103.4, 64.5, 36.7, 35.8; IR (KBr) 3325, 2907, 1577, 1439 cm^{-1}; MS (MALDI-TOF) *m/z* 534.4 $[M + H]^+$, 556.5 $[M + Na]^+$. Anal. Calcd for $C_{30}H_{27}N_7O_3$: C, 67.53; H, 5.10; N, 18.38. Found: C, 67.16; H, 5.01; N, 18.21.

Synthesis of Biscalix[1]arene[4]pyridine 14′. To a mixture of **13** (1066 mg, 2 mmol) and Cs_2CO_3 (978 mg, 3 mmol) in dried CH_2Cl_2 (100 mL) was added a solution of malonyl dichloride **2″** (Scheme S2 in Supporting Information) (169 mg) in dried CH_2Cl_2 (50 mL) for 3 h at 0 °C under argon protection. After 9 h of stirring, water (100 mL) was added, and the resulting mixture was stirred for 0.5 h. Then the aqueous phase was extracted with CH_2Cl_2 three times (100 mL × 3), and the organic phase was dried with anhydrous Na_2SO_4. The residue, after removal of the solvent, was chromatographed on a silica gel column to give pure product **14′** (670 mg, 59%) as a yellow solid: mp 120−121 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (t, J = 7.9 Hz, 4H), 7.47 (t, J = 2.1 Hz, 2H), 7.37 (t, J = 8.0 Hz, 4H), 6.95 (d, J = 2.1 Hz, 4H), 6.60 (d, J = 7.9 Hz, 4H), 6.56 (d, J = 8.0 Hz, 8H), 6.36 (d, J = 8.0 Hz, 4H), 5.19 (s, 4H), 3.54 (s, 2H), 3.40 (s, 6H), 3.38 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 161.0, 156.8, 156.1, 155.4, 154.4, 140.6, 138.2, 137.1, 116.0, 114.3, 108.4, 107.5, 106.7, 103.4, 66.4, 41.4, 36.7, 35.9; IR (KBr) 1755, 1738, 1593, 1568, 1435 cm^{-1}; MS (MALDI-TOF) m/z 1135.7 $[M + H]^+$. Anal. Calcd for $C_{63}H_{54}N_{14}O_8$ $[M + H]^+$: 1135.4322. Found: 1135.4323 $[M + H]^+$.

Synthesis of Calix[1]arene[4]pyridine−C_{60} Triad 14. Under argon protection, a mixture of C_{60} (200 mg, 0.278 mmol) and **14′** (235 mg, 0.208 mmol) in dried toluene (400 mL) was stirred until the C_{60} was thoroughly dissolved. The flask was covered with kitchen foil to avoid light irradiation. After a solution of CBr_4 (1152 mg, 3.470 mmol) in dried toluene was added, a solution of DBU (1055 mg, 6.940 mmol) in dried toluene was injected slowly for 2 h. After 6 h, the reaction was completed, and water (300 mL) was added. The organic phase was separated and dried with anhydrous Na_2SO_4. After filtration and removal of solvent, the residue was chromatographed on a silica gel column first with CS_2 to remove the unconsumed C_{60} and then with a mixture of CS_2 and CH_2Cl_2 (2:1) as the mobile phase to give pure **14** (163 mg, 42%) as a dark brown solid: mp 226−227 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (t, J = 2.2 Hz, 2H), 7.50 (t, J = 7.9 Hz, 4H), 7.35 (t, J = 8.0 Hz, 4H), 7.07 (d, J = 2.0 Hz, 4H), 6.58 (d, J = 8.2 Hz, 4H), 6.55 (d, J = 8.6 Hz, 4H), 6.52 (d, J = 8.1 Hz, 4H), 6.33 (d, J = 8.0 Hz, 4H), 5.51 (s, 4H), 3.39 (s, 6H), 3.37 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2, 161.0, 156.9, 156.2, 155.4, 154.4, 145.16, 145.10, 145.03, 144.89, 144.83, 144.62, 144.54, 143.7, 142.91, 142.84, 142.1, 141.7, 140.87, 140.68, 139.0, 138.2, 136.5, 116.7, 114.9, 108.4, 107.6, 106.7, 103.3, 71.1, 68.1, 36.8, 35.8; IR (KBr) 1751, 1593, 1568, 1434 cm^{-1}; MS (MALDI-TOF) m/z 1854.4 $[M + H]^+$. Anal. Calcd for $C_{123}H_{52}N_{14}O_8$ $[M + H]^+$: 1853.4130. Found: 1853,4165 $[M + H]^+$.

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Supporting Information Available: Experimental details and characterizations of products, ^{1}H and ^{13}C NMR spectra of products, UV−vis and fluorescence spectra, fluorescence titration spectra, and variable-temperature NMR of **11** and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.