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Reductive Benzylation of C_{70} Imidazoline with a Bulky Addend

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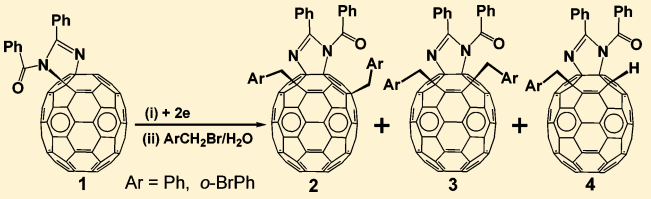
Supporting Information

ABSTRACT: Reductive benzylation of C_{70} imidazolines bearing a bulky addend has been carried out under conditions similar to that reported for C_{60} analogues. However, different from the reaction of C_{60} analogues, the reaction of C_{70} imidazolines not only results in adducts with 1,2,3,16-configuration due to the steric effect, but also a considerable amount of dibenzylated and monobenzylated products with 1,2,3,4-configuration, demonstrating a reactivity difference between C_{60} and C_{70}. Interestingly, the anions of the 1,2,3,16-C_{70} adduct are rather stable as shown by the electrochemical study, which is in contrast to the anions of 1,2,3,16-C_{60} counterparts, and can be rationalized by the electronic structure difference between C_{70} and C_{60} derivatives.

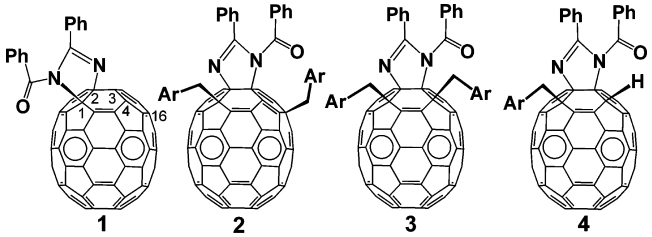


INTRODUCTION

The pursuit of novel fullerene derivatives has always been of interest and challenging,[1] as it would not only reveal new reactivity of these 3D carbon cages but may also discover new fullerene derivatives with unique properties for potential applications such as organic electronic materials.[2] Recently, Wang and our group have independently studied the reductive benzylation of C_{60} heterocycles (indoline and imidazoline) bearing a bulky addend, where a rare type of electronically unfavored 1,2,3,16-C_{60} adducts are obtained effectively due to the steric factors.[3,4] However, to the best of our knowledge, no C_{70} adducts with the 1,2,3,16-configuration have been reported so far, even though C_{70} has exhibited a similar but a more complicated reactivity with respect to that of C_{60}, due to the lowered symmetry of the molecule.[5,6]

Herein, we report the reductive benzylation of a 1,2-imidazolino[70]fullerene (**1** in Scheme 1),[7] which bears a bulky benzoyl group at the amino nitrogen atom, with the amino and imino nitrogen atoms at C1 and C2, respectively.[8] The reaction results in the first C_{70} adduct with a 1,2,3,16-configuration (**2** in Scheme 1) due to the steric effect, similar to the case when C_{60} derivatives with bulky addends are used.[3,4] However, different from the reaction of C_{60} analogues, a considerable amount of 1,2,3,4-C_{70} adducts (**3** and **4** in Scheme 1) are also formed; more interestingly, the 1,2,3,16-C_{70} adduct exhibits a good electrochemical stability, which is in sharp contrast to the case of 1,2,3,16-C_{60} counterparts, demonstrating a unique electronic difference between C_{60} and C_{70}.

Scheme 1. Illustrated Structures for the Compounds 1−4



RESULTS AND DISCUSSION

Reductive Benzylation of 1. Compound **1** was obtained with procedures reported previously.[7] The cyclic voltammetry measurement of **1** (Figure S1 in the Supporting Information [SI]) shows a quasi-reversible wave for the first redox process with $E_{1/2}$ at −0.49 V vs SCE (saturated calomel electrode), and an irreversible wave for the second redox process, as evidenced by the reduced anodic current and an unusually large peak separation (580 mV) between the peak potentials of the reduction (−0.89 V) and oxidation (−0.31 V) waves. The result is similar to that of C_{60} imidazoline[4] and C_{60}/C_{70} oxazoline,[9] indicating that the singly reduced **1** is stable, but the doubly reduced **1** likely undergoes a heterocyclic ring opening.

Compounds **2**, **3**, and **4** were obtained by benzylation of the doubly reduced **1**, which was generated by controlled-potential bulk electrolysis in PhCN containing 0.1 M TBAP (tetra-*n*-butylammonium perchlorate) with the potential set at −1.0 V vs SCE. The reaction was carried out by adding $ArCH_2Br$ (Ar = Ph and *o*-BrPh, n_{ArCH_2Br}:n_1 = 60:1) into $\mathbf{1}^{2-}$ solution under Ar and stirring, with the reaction time of 3 h at rt. The sterically favored 1,2,3,16-adducts of C_{70} (compounds **2a** and **2b**) were obtained as shown by the HPLC traces (Figures S2 and S17 in

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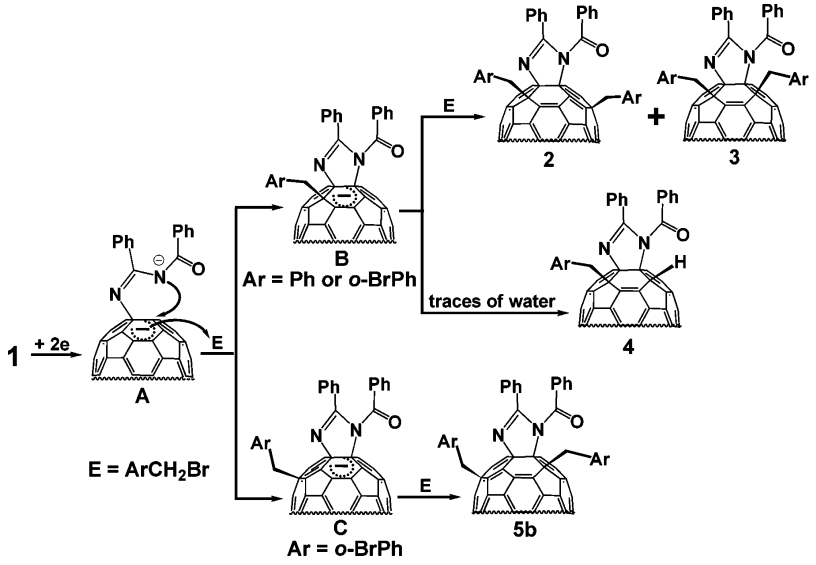
Scheme 2. Proposed Mechanism for the Reaction of the Doubly Reduced C_{70} Imidazoline with $ArCH_2Br$



the SI); however, different from the cases of the C_{60} analogues,[3,4] the reaction also results in a significant amount of dibenzylated and monobenzylated imidazolino C_{70} derivatives with the 1,2,3,4-configuration (compounds **3a**, **4a**, and **4b**), suggesting that first, there is likely more space room in the polar region of C_{70} compared with C_{60}, which may decrease the steric effect between bulky addends, consistent with our previous observation that the C2-phenyl of C_{70} has a lower rotational barrier than the benzyl located at the C_{60} cage;[10] and second, the C1−H of C_{70} is less acidic than C_{60}−H, which may promote the formation of organohydro[70]fullerenes by protonation with the traces of water in the solvent,[11] in agreement with the upper field shift of the fullerenyl hydrogen atom in 1,2-HBnC_{70} (4.07 ppm) compared with that in 1,2-HBnC_{60} (6.65 ppm).[11,12] Under typical conditions, the reactions afford **2a**, **3a**, and **4a** with a yield of 20%, 8%, and 28%, respectively, and **2b**, **3b**, and **4b** with a yield of 29%, 3%, and 23% respectively. In addition, about 2% of **5b** (see Scheme 2 for structure), which is also a 1,2,3,16-regioisomer but with the aryl group position switched with respect to **2b**, is obtained when bulkier *o*-BrPh is present, consistent with the result of C_{60} analogues.[4] Notably, a significant amount of C_{70} was also obtained from the reaction due to the decomposition of $\mathbf{1}^{2-}$.

The structures of **3** and **4** are first established before probing into the structure of **2**. The key evidence arise from the UV−vis (Figures S7, S12, S22, and S26 in the SI) and HMBC NMR spectra of **3a** and **4a** (Figures S11 and S16 in the SI). Absorptions typical for the 1,2,3,4-C_{70} regioisomer are shown at 345, 374, 432, 468, 535, and 690 nm,[9b] suggesting that these two compounds are 1,2,3,4-adducts as the UV−vis absorptions are sensitive toward the structure of the compound, rather than the type of the addends.[13] The HMBC NMR spectra show that in compound **3a**, the sp^3 C_{70} carbon atom respectively bound to the imino and amino nitrogen atom (85.22 or 81.35 ppm) has a correlation with the methylene protons at 3.75, 3.56 ppm (ABq) and 4.31, 2.30 ppm (ABq); as in compound **4a**, the imino N-bound sp^3 C_{70} carbon atom (82.21 ppm) is correlated with the methylene protons at 3.89, 3.21 ppm (ABq), while the amino N-bound sp^3 C_{70} carbon atom (75.45 ppm) has a correlation with the fullerenyl hydrogen atom at 4.27 ppm, demonstrating explicitly that compounds **3a** and **4a** are both 1,2,3,4-adducts. Notably, the amino and imino nitrogen atoms are positioned at C1 and C2 respectively in **1** as shown by the X-ray single-crystal diffractions,[8] indicating that the amino nitrogen atom would relocate from C1 to C3 during the conversion from **1** to **3a** and **4a**, consistent with the results of C_{60} imidazoline[4] and 1,2-C_{70} oxazoline,[9b] where the amino nitrogen atom and the heteroatom at C1 of C_{70} migrate. In addition, previous work has shown that the benzylation of the doubly reduced C_{60} imidazoline[4] and C_{60}/C_{70} oxazolines[9] is undertaken via a stepwise manner, with the addition of the first benzyl at the [6,6]-carbon adjacent to the remaining imino N−C_{2n} (n = 30 or 35) bond, followed by the addition of the second group at the ortho or para position with respect to the relocated X−C_{2n} (X = N or O) bond depending on the size of the addend. It therefore indicates that the benzyl or the fullerenyl hydrogen next to the amino N−C_{70} bond is the group added during the second step. Compounds **3b** and **4b** are also assigned as the 1,2,3,4-adducts because they show similar UV−vis and NMR spectral features to those of **3a** and **4a**.

As for compound **2a**, the imino N-bound sp^3 C_{70} carbon atom (89.38 ppm) exhibits a correlation with the methylene protons at 4.51 and 3.49 ppm (ABq) (Figure S6 in the SI for HMBC NMR), indicating that one benzyl is located next to the imino N−C_{70} bond, similar to the case of **3a** and **4a**. However, no correlation is shown between the amino N-bound sp^3 C_{70} carbon (73.87 ppm) and the other set of methylene protons, indicating explicitly that the other benzyl is not positioned at the ortho site with respect to the amino N−C_{70} bond in **2a**. The result suggests that compounds **2a** and **3a** are likely formed via the same monobenzylated imidazolino C_{70} monoanion intermediate, where the first added benzyl is more preferential to being placed next to the remaining imino N−C_{70} bond due to the electronic factor.[4,9] The bulky benzoyl group at the amino nitrogen atom in the imidazoline plays an important role in directing the addition site of the second benzyl for the formation of **2a**, which results in the 1,2,3,16-regioisomer by placing the second benzyl at the para site with respect to the amino N−C_{70} bond, consistent with the benzylation of bulky C_{60} heterocycles.[3,4] Notably, due to the availability of more space room in the polar region of C_{70}, a significant amount of **3a** with the 1,2,3,4-configuration can also

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be formed by placing the second benzyl at the ortho site with respect to the amino N−C_{70} bond. Further examination with the more sterically demanding *o*-BrPh group affords more **2b** and much less **3b**, confirming that the formation of the 1,2,3,16-regioisomer of C_{70} is indeed a result of steric hindrance between the bulky addends. Figure 1 shows the UV−vis

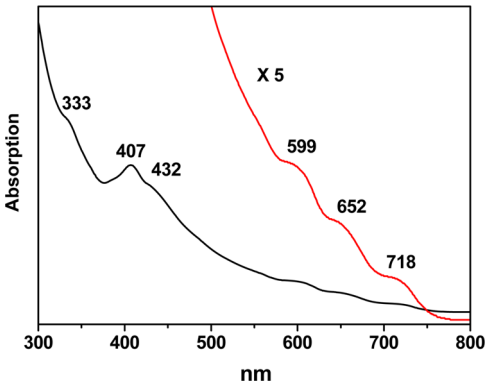

Figure 1. UV−vis spectrum of **2a** recorded in toluene.

spectrum of **2a**, which has one major absorption band at around 407 nm, and shoulder bands at around 333, 432, 599, 652, and 718 nm. Similar UV−vis absorptions are also shown for **2b** (Figure S18 in the SI). A small amount of **5b**, whose structure was determined to be also a 1,2,3,16-regioisomer on the basis of UV−vis absorptions, was obtained when *o*-$BrPhCH_2Br$ was used (Figure S17 in the SI for HPLC). However, the structure of **5b** is different from those of **2a** and **2b** as the ^{1}H NMR indicates (Figure S31 in the SI), in which the addition pattern for the two benzyls is likely switched, resembling the case of C_{60} imidazoline.[4]

A possible mechanism for the reaction of the doubly reduced C_{70} imidazoline with $ArCH_2Br$ (Ar = Ph or *o*-BrPh) is shown in Scheme 2, which is essentially identical to that of C_{60} imidazoline[4] and C_{70} oxazoline analogues.[9b] The amino N−C_{70} bond at C1 is cleaved during the reduction, while the imino N−C_{70} bond remains intact to afford intermediate **A**. The addition of the first aryl group takes place preferentially at the [6,6]-ortho position with respect to the remaining imino N−C_{70} bond, accompanied by the closure of the imidazoline ring. The exhibited regioselectivity for the first aryl group is in agreement with the reactivity of the singly bonded C_{70} intermediates with the addends in the apical carbon atom,[6c,11] as the ortho addition is electronically favored with no [5,6]-double bond formed in the structure.[14] As a result of more available space in the polar region of C_{70}, compound **3a** with 1,2,3,4-configuration can be formed in significant amount. A considerable amount of monobenzylated **4** is also formed via the protonation of intermediate **B** with traces of water in the solvent due to the less acidity of C_{70}−H. In addition, due to the existence of large steric hindrance, a considerable amount of the second aryl group is added with a para manner and results in the 1,2,3,16-regioisomer (**2**), especially when the bulkier *o*-$BrPhCH_2$ is used. Ab initio Hartree−Fock calculations at the HF/6-311G(d)//HF/6-31G level with Gaussian09 program predict that the **2a** is more stable than **3a** by about 2.0 kcal/mol (−3909.2750 vs −3909.2718 hartree), consistent with the preferential formation of **2** over **3**. Moreover, a small amount of **5b**, another type of 1,2,3,16-regioisomer, is formed from the reaction when the sterically demanding *o*-$BrPhCH_2$ is placed at the C_{70} cage, because a small amount of *o*-$BrPhCH_2$ would take a para manner during the first addition step to generate intermediate **C** due to the steric hindrance.

Unusual Electrochemical Stability of the Sterically Favored Regioisomer 2. Figure 2 displays the cyclic

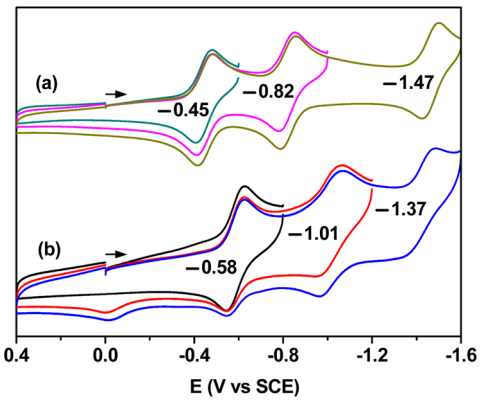

Figure 2. Cyclic voltammograms of (a) **2a** and (b) **3a** in PhCN containing 0.1 M TBAP at rt. Scan rate = 0.1 V/s. The arrows indicate the starting potential (0 V) and the scan direction for the measurements.

voltammograms of **2a** and **3a**, which reveal first that compound **2a** is more electron deficient than **3a** by having a more positive $E_{1/2}$ potential (−0.45 vs −0.58 V), consistent with the result for C_{60} analogues.[4] Such an anodic potential shift of **2a** has been rationalized by the LUMO localization at the double bond in the pentagons,[15] in agreement with the introduction of a [5,6]-double bond in **2a**, and is supported by the calculations, which show that the LUMO in **2a** is indeed more localized at the [5,6]-double bond compared with the well delocalized one in **3a** (Figure S32 in the SI). Second, the cyclic voltammograms show that the anions of sterically favored regioisomer **2a** are very stable, as shown by the reversibility of the redox waves. Similar electrochemical stability is also observed for **2b** by the cyclic voltammetry measurement (Figure S33 in the SI). The exhibited electrochemical stability for the 1,2,3,16-C_{70} regioisomer is quite intriguing as previous work on C_{60} analogues has shown that the stability of the anionic species of C_{60} derivatives is rather dependent on the intrinsic electronic structure, where only the electronically favored 1,2,3,4-adducts are electrochemically stable, while the sterically favored 1,2,3,16-regioisomer is electrochemically instable, even though the sterically favored regioisomer may be more stable than the electronically favored one in neutral form.[4]

The distinct electrochemical stability of **2** indicates a unique electronic structural feature of C_{70}. As for C_{70} derivatives, the equatorial hexagons have a strong benzoid nature,[6a] which may cause the [5,6]-bond in the equatorial hexagons to possess a more double bond nature. Indeed, ab initio calculation at the HF/6-31G level on $\mathbf{2a}^{2-}$ predicts a short bond length of 1.430 Å for the equatorial [5,6]-bond located within the pentagon that bears the polar [5,6]-double bond, which matches well with the other two short bonds (1.389 and 1.408 Å) in the equatorial hexagon, suggesting a cyclopentadiene structure is formed in **2a** as shown in Figure 3. In contrast, no cyclopentadiene structure is formed in the C_{60} analogue, where the double bonds are rather localized at the [6,6]-bonds as predicted by the same calculation shown in Figure 3.

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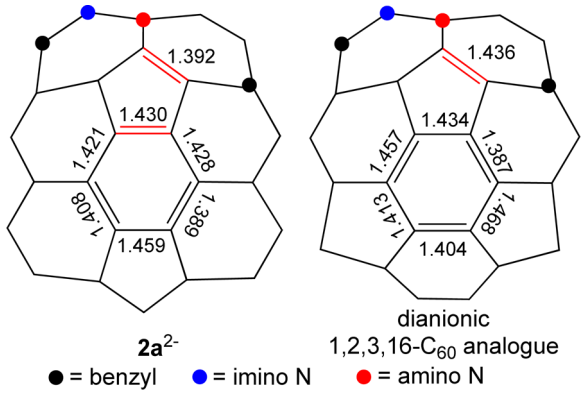

Figure 3. Schematic illustrations of the partial structures of the dianionic species of **2a** and 1,2,3,16-C_{60} analogue with labeling of partial calculated bond lengths (Å). The double bonds are drawn only in the discussed pentagon and hexagon for clarity.

Previous work on a 1,6-adduct of C_{60} has shown that the molecule has a 1,3-butadiene structure, composed of two neighboring [5,6]-double bonds, which plays a key role in stabilizing the cationic species of the compound by a conjugation effect.[16] Similarly, the cyclopentadiene structure in **2a** can also stabilize the anions of the compound by delocalizing the acquired charges, which would otherwise localize at the isolated [5,6]-double bond in the 1,2,3,16-C_{60} analogue and induces instability, due to the absence of such conjugated cyclopentadiene structure caused by the electronic structural difference between C_{60} and C_{70}.

CONCLUSION

In summary, novel C_{70} derivatives with 1,2,3,16-configuration have been obtained via the reductive benzylation of a C_{70} imidazoline bearing a bulky addend. Different from the result of C_{60} imidazoline, the reaction also affords a significant amount of dibenzylated or monobenzylated C_{70} derivatives with 1,2,3,4-configuration, indicating that there is likely more space room in the polar region of C_{70} to hold these bulky addends together, and the C_{70}–H is less acidic than the C_{60}–H. Interestingly, the sterically favored 1,2,3,16-C_{70} adduct exhibits a better electrochemical stability with respect to that of the 1,2,3,16-C_{60} analogue, which is attributed to the formation of the cyclopentadiene unit due to the benzoid nature of the equatorial hexagons, demonstrating an important difference of the electronic structure between C_{70} and C_{60} derivatives.

EXPERIMENTAL SECTION

General Methods. All reactions were carried out under an atmosphere of Ar. All reagents were obtained commercially and used without further purification, unless otherwise noted. Benzonitrile (PhCN) was distilled over P_2O_5 under vacuum at 305 K prior to use. Tetra-*n*-butylammonium perchlorate (TBAP) was recrystallized from absolute ethanol and dried under vacuum at 313 K prior to use. No data on the melting point of the products could be obtained, since the compounds would decompose before reaching the melting point.

Controlled-potential bulk electrolysis (CPE) was carried out on a potentiostat/galvanostat using an "H" type cell. Two platinum gauze electrodes (working and counter electrodes) were separated by a sintered glass frit. For CV measurements, a three-electrode cell was used and a glassy carbon and platinum wire were used as working electrode and counter electrode. In both controlled-potential bulk electrolysis and CV measurements, a saturated calomel electrode (SCE) was used as reference electrode. A fritted-glass bridge of low porosity which contained the solvent/supporting electrolyte mixture was used to separate the SCE from the bulk of the solution.

Preparation of Compounds 2a, 3a, and 4a. Typically, 58 mg (55 μmol) of compound **1** in 50 mL of freshly distilled PhCN solution containing 0.1 M TBAP was electrolyzed at −1.0 V vs SCE under Ar atmosphere. The potentiostat was switched off once the theoretical number of electrons required for reducing **1** to $\mathbf{1}^{2-}$ was achieved. Sixty-fold $PhCH_2Br$ (390 μL, 3.3 mmol) was added to the solution. The benzylation reaction was allowed to proceed for 3 h under Ar at rt. The solvent was removed under reduced pressure, and the residue was washed with methanol to remove TBAP. The crude product was put into toluene, and the soluble part was purified with HPLC by eluting a 70:30 v/v mixture of toluene/hexane over a semipreparative YMC-pack silica column (10 mm × 250 mm) at a flow rate of 3.7 mL/min with the detector wavelength set at 380 nm. Compounds **2a**, **3a**, and **4a** were obtained with an isolated yield of 20% (13.6 mg), 8% (5.5 mg), and 28% (17.7 mg), along with 7 mg of C_{70} produced by decomposition of **1** during the reaction. No data on the melting point of the C_{70} derivatives could be obtained, since the compounds would decompose before reaching the melting point.

Spectral Characterization of ***2a****:* positive ESI FT-ICR MS, *m*/*z* calcd for $C_{98}H_{25}N_2O^+$ $[M + H]^+$ 1245.19614, found 1245.19410; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.50–7.48 (m, 2H), 7.37 (d, 2H), 7.05–6.98 (m, 8H), 6.94 (t, 2H), 6.87 (t,2H), 6.83–6.79 (m, 4H); 4.62, 3.76 (ABq, 2H, J_{AB} = 12.5 Hz); 4.51, 3.49 (ABq, 2H, J_{AB} = 12.5 Hz); ^{13}C NMR (125 MHz, DMSO-d_6) δ 173.50 (C═O), 168.60 (1C), 166.16 (1C), 162.69 (1C), 157.63 (C═N), 157.32 (1C), 153.22 (1C), 151.86 (1C), 151.13 (1C), 151.08 (1C), 150.53 (1C), 149.88 (1C), 149.75 (1C), 149.66 (1C), 149.57 (1C), 149.20 (1C), 148.93 (1C), 148.84 (1C), 148.78 (1C), 148.74 (1C), 148.54 (1C), 148.31 (1C), 147.92 (1C), 147.83 (1C), 147.59 (1C), 147.54 (1C), 147.40 (1C), 147.26 (1C), 147.12 (1C), 146.78 (1C), 146.78 (1C), 146.48 (1C), 146.25 (1C), 145.95 (1C), 145.79 (1C), 145.69 (1C), 145.52 (1C), 145.39 (1C), 145.37 (1C), 145.19 (1C), 144.95 (1C), 144.58 (1C), 144.46 (1C), 144.14 (1C), 144.11 (1C), 143.89 (1C), 143.20 (1C), 142.98 (2C), 142.54 (1C), 142.33 (1C), 142.24 (1C), 141.28 (1C), 139.85 (1C), 139.31 (1C), 137.98 (1C, Ph), 136.82 (1C, Ph), 136.26 (1C), 135.29 (1C), 134.96 (1C), 134.54 (1C), 133.90 (1C), 132.78 (1C), 132.03 (1C, Ph), 131.95 (1C), 131.90 (1C), 131.88 (1C), 131.55 (1C), 131.47 (2C, Ph), 130.86 (2C, Ph), 130.45 (1C, Ph), 129.93 (1C), 129.23 (2C, Ph), 129.11 (1C, Ph), 128.74 (2C, Ph), 128.61 (1C, Ph), 128.24 (2C, Ph), 128.21 (2C, Ph), 128.15 (2C, Ph), 127.73 (2C, Ph), 127.35 (1C), 127.09 (1C, Ph), 126.74 (1C, Ph), 123.24 (1C), 89.38 (C–N═), 73.87 (C–N–), 60.71 (*C*–CH_2Ph), 58.03 (*C*–CH_2Ph), 45.10 (CH_2), 40.15 (CH_2); UV–vis (toluene): λ_{max} 333, 407, 432, 599, 652,718 nm.

Spectral Characterization of ***3a****:* positive ESI FT-ICR MS, *m*/*z* calcd for $C_{98}H_{25}N_2O^+$ $[M + H]^+$ 1245.19614, found 1245.19528; ^{1}H NMR (500 MHz, DMSO) δ 7.36 (d, 2H), 7.24 (d, 2H), 7.01, 7.00, 6.98–6.92 (m, 5H), 6.88 (t, 1H), 6.83–6.67 (m, 8H), 6.63 (t, 2H); 3.75, 3.56 (ABq, 2H, J_{AB} = 13.5 Hz), 4.31, 2.30 (ABq, 2H, J_{AB} = 12.0 Hz); ^{13}C NMR (150 MHz, DMSO) δ 170.18 (C═O), 164.21 (1C), 162.77 (1C), 159.42 (C═N), 152.31 (1C), 150.66 (1C), 150.49 (1C), 150.39 (1C), 150.11 (1C), 149.86 (1C), 149.84 (1C), 149.73 (1C), 149.62 (1C), 149.49 (1C), 149.26 (1C), 149.17 (2C), 148.86 (1C), 148.73 (1C), 148.71 (1C), 148.67 (1C), 148.58 (1C), 148.52 (2C), 148.50 (1C), 148.45 (1C), 148.38 (1C), 147.86 (1C), 147.81 (2C), 147.70 (2C), 147.62 (1C), 147.55 (1C), 147.09 (1C), 146.61 (1C), 146.44 (2C), 146.17 (1C), 145.46 (1C), 144.08 (2C), 143.15 (1C), 143.13 (1C), 142.86 (1C), 142.41 (1C), 141.91 (1C), 141.44 (1C), 141.11 (1C), 140.78 (1C), 140.47 (1C), 140.39 (1C), 139.06 (1C), 138.99 (1C), 137.86 (1C), 137.18 (1C, Ph), 136.29 (1C, Ph), 136.21 (1C), 134.66 (1C), 133.38 (1C), 133.05 (1C), 132.96 (1C), 131.85 (1C), 131.58 (1C), 131.53 (1C), 131.46 (1C), 131.38 (1C), 126.88 (1C), 131.30 (2C, Ph), 131.30 (1C, Ph), 131.10 (2C, Ph), 130.94 (1C, Ph), 130.60 (1C), 129.88 (1C, Ph), 129.24 (1C), 128.35 (1C, Ph), 128.15 (2C, Ph), 128.11 (2C, Ph), 127.59 (2C, Ph), 127.48 (2C, Ph), 127.15 (4C, Ph), 126.24 (1C, Ph), 126.09 (1C, Ph), 85.22 (C–N═), 81.35 (C–N–), 58.56 (*C*–CH_2Ph), 58.13 (*C*–CH_2Ph),

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44.19 (CH_2), 41.15 (CH_2); UV−vis (toluene): λ_{max} 347, 377, 433, 468, 537, 692 nm.

Spectral Characterization of ***4a****:* positive ESI FT-ICR MS, *m*/*z* calcd for $C_{91}H_{19}N_2O^+$ $[M + H]^+$ 1155.14919, found 1155.14773; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.17−7.15 (m, 2H), 7.09 (d, 2H), 6.98−6.95 (m.1H), 6.93−6.89 (m, 3H), 6.88−6.84 (m, 4H), 6.81−6.78 (m, 3H), 4.27 (s, 1H); 3.89, 3.21 (ABq, 2H, J_{AB} = 13.5 Hz) ; ^{13}C NMR (125 MHz, DMSO-d_6) δ 168.59 (C═O), 162.57 (1C), 162.46 (1C), 157.01 (C═N), 155.26 (1C), 151.47 (1C), 151.06 (2C), 151.03 (2C), 150.89 (1C), 150.60 (2C), 150.41 (1C), 150.26 (1C), 150.14 (1C), 149.92 (1C), 149.81 (1C), 149.73 (2C), 149.66 (2C), 149.57 (2C), 149.41 (1C), 149.32 (1C), 149.23 (1C), 149.04 (1C), 148.99 (1C), 148.90 (1C), 148.83 (1C), 148.67 (1C), 148.53 (1C), 148.15 (1C), 147.81 (2C), 147.50 (1C), 147.35 (1C), 147.07 (1C), 146.94 (1C), 146.76 (1C), 146.56 (1C), 146.09 (1C), 144.57 (1C), 144.53 (1C), 144.38 (1C), 144.38 (1C), 143.66 (1C), 143.55 (1C), 142.65 (1C), 142.63 (1C), 142.06 (1C), 141.14 (1C), 141.08 (1C), 141.04 (1C), 140.97 (1C), 140.19 (1C), 140.16 (1C), 139.39 (1C), 137.47 (1C, Ph), 135.60 (1C, Ph), 135.42 (1C), 134.53 (1C), 133.54 (1C), 133.45 (1C), 132.13 (1C), 132.09 (1C), 131.92 (1C), 131.89 (1C), 131.86 (1C), 131.57 (1C, Ph), 131.40 (1C, Ph), 130.99 (1C, Ph), 129.84 (2C, Ph), 129.04 (2C, Ph), 128.45 (2C, Ph), 127.87 (2C, Ph), 127.76 (4C, Ph), 126.62 (1C, Ph), 82.21 (C−N═), 75.45(C−N−), 58.72 (C−CH_2Ph), 50.77 (1C, sp^3, C−H), 43.59 (CH_2); UV−vis (toluene): λ_{max} 345, 374, 432, 468, 535, 690 nm.

Preparation of Compounds 2b, 3b, 4b, and 5b. The procedures were similar to those for preparation of **2a**, **3a**, and **4a**, except 50 mg of **1** (47 μmol) was used and *o*-BrPhCH$_2$Br (700 mg, 2.8 mmol) was used instead of PhCH$_2$Br. Compounds **2b**, **3b**, **4b**, and **5b** were obtained with an isolated yield of 29% (19.2 mg), 3% (2 mg), 23% (13.4 mg), and 2% (1.3 mg), along with 6 mg of C_{70} produced by decomposition of **1** during the reaction. No data on the melting point of the C_{70} derivatives could be obtained, since the compounds would decompose before reaching to the melting point.

Spectral Characterization of ***2b****:* positive ESI FT-ICR MS, *m*/*z* calcd for $C_{98}H_{23}Br_2N_2O^+$ $[M + H]^+$ 1401.01716, found 1401.01516; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.51−7.50 (m, 2H), 7.47−7.44 (m, 3H), 7.34 (d, 1H), 7.12−7.08 (m, 2H), 7.00−6.99 (m, 4H), 6.94−6.91 (m, 3H), 6.81 (t, 3H), 6.74−6.70 (m, 2H); 4.78, 4.13 (ABq, 2H, J_{AB} = 13.0 Hz); 4.55, 3.92 (ABq, 2H, J_{AB} = 13.0 Hz); ^{13}C NMR (150 MHz, DMSO-d_6) δ 172.75 (C═O), 168.23 (C═N), 165.55 (1C), 161.57 (1C), 157.20 (1C), 156.48 (1C), 152.13 (1C), 151.26 (1C), 150.61 (1C), 150.45 (1C), 149.89 (1C), 149.40 (1C), 149.21 (1C), 149.11 (1C), 148.95 (1C), 148.60 (1C), 148.34 (3C), 148.29 (1C), 148.20 (1C), 147.99 (1C), 147.76 (1C), 147.38 (1C), 147.24 (1C), 146.98 (1C), 146.80 (1C), 146.77 (1C), 146.58 (1C), 146.27 (1C), 146.15 (1C), 145.94 (1C), 145.66 (1C), 145.54 (1C), 145.11 (1C), 145.02 (1C), 144.87 (1C), 144.73 (1C), 144.66 (1C), 144.57 (1C), 144.52 (1C), 143.97 (1C), 143.67 (1C), 143.48 (1C), 143.33 (1C), 143.30 (1C), 142.53 (1C), 142.47 (1C), 142.31 (1C), 141.92 (3C), 141.36 (1C), 140.58 (1C), 139.22 (1C), 138.85 (1C), 137.26 (1C, Ph), 136.29 (1C, Ph), 135.68 (1C, Ph), 134.60 (1C), 134.37 (1C), 134.01 (1C), 133.33 (1C, Ph), 132.74 (1C, Ph), 132.61 (1C, Ph), 132.22 (1C), 132.15 (1C, Ph), 131.71 (1C), 131.46 (1C, Ph), 131.34 (1C), 131.29 (1C), 131.03 (1C), 129.92 (1C, Ph), 129.26 (1C), 128.80 (2C, Ph), 128.68 (1C), 128.43 (1C), 128.20 (2C, Ph), 128.20 (1C, Ph), 127.69 (1C, Ph), 127.63 (2C, Ph), 127.57 (2C, Ph), 126.49 (1C, Ph), 126.39 (1C, Ph), 126.29 (1C, Ph), 126.26 (1C, Ph), 125.88 (1C, Ph), 122.85, 88.93 (C−N═), 73.23 (C−N−), 60.02 (C−CH_2Ph), 57.00 (C−CH_2Ph), 43.26 (CH_2), 38.05 (CH_2); UV−vis (toluene): λ_{max} 334, 407, 432, 597, 652, 723 nm.

Spectral Characterization of ***3b****:* positive ESI FT-ICR MS, *m*/*z* calcd for $C_{98}H_{23}Br_2N_2O^+$ $[M + H]^+$ 1401.01716, found 1401.01476; ^{1}H NMR (600 MHz, acetone-d_6) δ 6.96 (d, 2H), 6.82 (d, 2H), 6.78 (d, 1H), 6.64−6.62 (m, 2H), 6.58 (d, 1H), 6.54 (d, 1H), 6.50−6.48 (m, 5H), 6.40 (t, 1H), 6.27−6.22 (m, 2H), 6.18 (t, 1H); 4.30, 2.50 (ABq, 2H, J_{AB} = 12.0 Hz); 3.98, 2.90 (ABq, 2H, J_{AB} = 12.0 Hz); UV−vis (toluene): λ_{max} 347, 375, 433, 470, 536, 695 nm.

Spectral Characterization of ***4b****:* positive ESI FT-ICR MS, *m*/*z* calcd for $C_{91}H_{18}BrN_2O^+$ $[M + H]^+$ 1233.05970, found 1233.06037; ^{1}H NMR (600 MHz, DMSO-d_6), δ 7.28 (d, 2H), 7.24 (d, 2H), 7.16 (d, 1H), 7.05 (d, 1H), 7.01 (t, 1H), 6.94−6.90 (m, 5H), 6.86 (t, 1H), 6.70 (t, 1H), 4.30 (s, 1H); 3.96, 3.49 (ABq, 2H, J_{AB} = 13 Hz); ^{13}C NMR (150 MHz, DMSO-d_6), δ 168.10 (C═O), 161.98 (1C), 161.07 (C═N), 156.64 (1C), 155.01 (1C), 151.04 (1C), 150.72 (1C), 150.58 (1C), 150.55 (1C), 150.50 (1C), 150.10 (1C), 150.00 (1C), 149.96 (1C), 149.92 (1C), 149.75 (1C), 149.46 (1C), 149.37 (1C), 149.29 (1C), 149.23 (1C), 149.15 (1C), 149.15 (2C), 149.12 (1C), 148.92 (1C), 148.72 (1C), 148.55 (1C), 148.39 (1C), 148.25 (1C), 148.18 (1C), 148.10 (1C), 148.09 (1C), 147.66 (1C), 147.38 (1C), 147.32 (1C), 146.90 (1C), 146.80 (2C), 146.56 (1C), 146.43 (1C), 146.28 (1C), 146.00 (1C), 145.32 (1C), 144.77 (1C), 144.65 (1C), 144.05 (1C), 143.90 (1C), 143.18 (1C), 143.07 (1C), 142.22 (1C), 142.04 (1C), 141.64 (1C), 140.54 (1C), 140.52 (2C), 140.48 (1C), 140.04 (1C), 139.29 (1C), 138.76 (1C), 136.25 (1C), 135.31 (1C), 134.97 (1C), 133.88 (1C), 133.00 (1C), 132.84 (1C, Ph), 132.55 (1C, Ph), 131.62 (1C), 131.60 (1C), 131.46 (1C), 131.37 (1C), 131.37 (1C), 131.18 (1C, Ph), 130.90 (1C, Ph), 130.20 (1C, Ph), 129.43 (1C, Ph), 128.57 (2C, Ph), 128.37 (1C, Ph), 127.95 (2C, Ph), 127.67 (1C, Ph), 127.38 (4C, Ph), 126.31 (1C, Ph), 126.24 (1C, Ph), 81.76 (C−N═), 75.04 (C−N−), 57.80 (C−CH_2Ph), 50.16 (sp^3, C−H), 41.08 (CH_2) ; UV−vis (toluene): λ_{max} 344, 375, 432, 469, 536, 695 nm.

Spectral Characterization of ***5b****:* positive ESI FT-ICR MS, *m*/*z* calcd for $C_{98}H_{23}Br_2N_2O^+$ $[M + H]^+$ 1401.01716, found 1401.01926; ^{1}H NMR (600 MHz, acetone-d_6) δ 7.00 (d, 2H), 6.94 (d, 2H), 6.81−6.78 (m, 2H), 6.62 (d, 1H), 6.58 (d, 1H), 6.54−6.51 (m, 7H), 6.40 (t, 2H), 6.22 (t, 1H); 4.55, 3.40 (ABq, 2H, J_{AB} = 10.2 Hz); 3.47, 3.40 (ABq, 2H, J_{AB} = 13.2 Hz); UV−vis (toluene): λ_{max} 334, 405, 431, 600, 653, 718 nm.

Computational Methods. The structures of **2a**, **3a**, and **2a**$^{2-}$ were optimized with Gaussian09 at the HF/6-31G level, followed by harmonic frequency calculations at the same level to confirm them as the energy minima. The energies of **2a** and **3a** were obtained at the HF/6-311G(d) level.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

HPLC traces, spectra of the new compounds, and calculation details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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