

Novel photoswitchable dielectric properties on nanomaterials of electronic core-shell γ -FeO_x@Au@fullerosomes for GHz frequency applications

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Supporting Information

Material Preparation

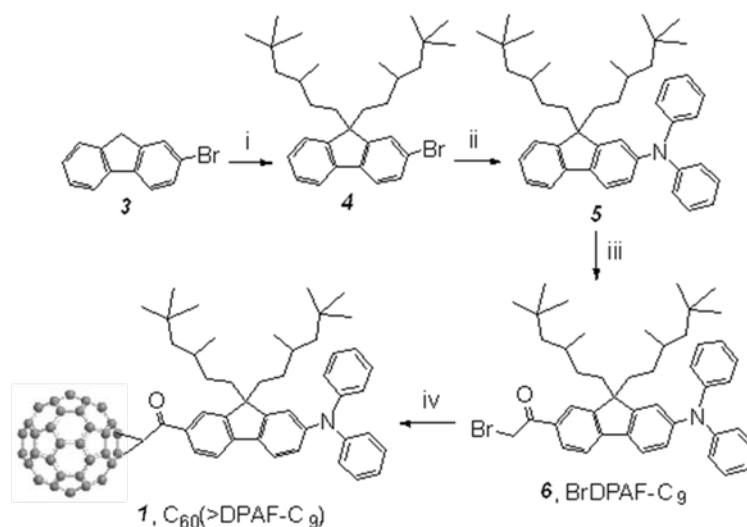


Figure S1. Synthesis of C₆₀-(antenna)_x nanostructures **1**. Reagent and reaction conditions: i. 1-C₉H₃₇-OMs, *t*-BuOK in THF, 0 °C–r.t., 4 h; ii. diphenylamine, tris(dibenzylideneacetone)dipalladium(0) (cat.), *rac*-BINAP (cat.), *t*-BuONa, toluene, 110 °C, 8.0 h; iii. α -bromoacetyl bromide, AlCl₃, ClCH₂CH₂Cl, 0 °C, 4.0 h; iv. C₆₀, DBU, toluene, r.t., 5.0 h.

Synthesis of 9,9-di(3,5,5-trimethylhexyl)-2-bromofluorene 4. To a solution of 2-bromofluorene **3** (4.0 g, 16.3 mmol) in dry tetrahydrofuran (150 mL) was added potassium *t*-butoxide (5.5 g, 49.0 mmol) resulting in orange suspension. The mixture was stirred at room temperature for a period of 20 min. The suspension was cooled below 10 °C and added a tetrahydrofuran solution of 3,5,5-trimethylhexyl mesylate (11.0 g, 49.0 mmol) dropwise over a period of 30 min. Gradual color change of the reaction mixture from deep red to deep purple was observed by stirring overnight. At the end of the reaction, it was quenched by addition of water and extracted with ethyl acetate, dried over sodium sulfate, and concentrated in vacuo to give the crude product which was purified by column chromatography (silica gel, hexane as eluent). A chromatographic fraction corresponding to $R_f = 0.8$ on TLC (SiO_2 , hexane as eluent) was isolated to afford 9,9-di(3,5,5-trimethylhexyl)-2-bromofluorene **4** (7.6 g) as colorless oil in a yield of 94%. Spectroscopic data of **4**: FAB⁺-MS calcd for $^{12}\text{C}_{31}^{1}\text{H}_{45}^{79,9}\text{Br}_1$ m/z 497; found, m/z 496 and 498; FT-IR (KBr) ν_{max} 3060 (w), 2964 (vs), 2919 (s), 2876 (s), 2852 (s), 1598 (w), 1570 (w), 1443 (vs), 1404 (s), 1378 (s), 1255 (m), 1132 (m), 1061 (m), 1004 (m), 876 (m), 823 (s), 781 (s), 767 (vs), 733 (vs), 569 (m), and 418 (s) cm^{-1} ; ^1H NMR (500 MHz, CDCl_3 , ppm) δ 7.65–7.62 (m, 1H), 7.55–7.51 (m, 1H), 7.46–7.41 (m, 2H), 7.35–7.27 (m, 3H), 2.1–1.8 (m, 4H), and 1.35–0.38 (m, 34H); ^{13}C NMR (500 MHz, CDCl_3 , ppm) δ 152.8, 150.2, 140.2, 140.1, 129.8, 127.5, 126.9, 126.1, 122.8, 121.0, 120.9, 119.7, 55.1, 50.7, 50.7, 37.7, 32.8, 32.7, 30.9, 29.9, 29.5, 29.4, 22.4, and 22.4.

Synthesis of 9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene 5. A mixture of 9,9-di(3,5,5-trimethylhexyl)-2-bromofluorene **4** (5.9 g, 11.9 mmol), diphenylamine (2.4 g, 14.2 mmol) tris(dibenzylideneacetone)dipalladium(0) (27 mg, 0.25 mmol%), *rac*-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP, 89 mg, 0.75 mmol%) and sodium *t*-butoxide (1.6 g, 16.6 mmol) in dry toluene (150 mL) was heated to refluxing temperatures for a period of 8.0 to 10.0 h under nitrogen atmosphere. After cooling the reaction mixture to room temperature, it was diluted with diethyl ether (60 mL), washed with brine (80 mL), and further washed with water. The diethyl ether layer was dried over sodium sulfate and concentrated in vacuo to give the crude product, which was purified by column chromatography (silica gel) using hexane as eluent. A chromatographic fraction corresponding to $R_f = 0.6$ on TLC (SiO_2 , hexane as eluent) was isolated to afford 9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene **5** as colorless oil in 98% yield (6.8 g). Spectroscopic data of **5**: FAB⁺-MS calcd for $^{12}\text{C}_{43}^{1}\text{H}_{55}^{14}\text{N}_1$ m/z 585; found, m/z 585; ^1H NMR (500 MHz, CDCl_3 , ppm) δ 7.6–7.52 (m, 2H), 7.3–7.19 (m, 7H), 7.15–7.05 (m, 5H), 7.05–6.94 (m, 3H), 1.99–1.75 (m, 4H), and 1.29–0.38 (m, 34H); ^{13}C NMR (500 MHz, CDCl_3 ,

ppm) δ 151.9, 150.4, 148.0, 147.0, 140.9, 136.6, 129.2, 129.1, 126.7, 126.3, 124.1, 123.7, 122.6, 122.4, 120.3, 119.4, 119.1, 54.8, 50.9, 37.9, 33.1, 34.0, 30.9, 29.9, 29.4, 22.5, and 22.5.

Synthesis of 7- α -bromoacetyl-9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene BrDPAF-C₉, 6.

To a suspension of aluminum chloride (792 mg, 6.0 mmol) in 1,2-dichloroethane (30 ml) at 0 °C was added a solution of 9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene **5** (3.17 g, 5.4 mmol) in 1,2-dichloroethane (30 mL). It was then added by α -bromoacetyl bromide (0.57 ml, 6.5 mmol) over 10 min while maintaining the temperature of reaction mixture between 0–10 °C. The mixture was warmed to ambient temperature and stirred for an additional 4.0 h. At the end of the reaction, it was quenched by slow addition of water (100 mL) while maintaining the temperature below 45 °C. The organic layer was separated and washed sequentially with dil. HCl (1.0 N, 50 mL) and water (50 mL, 2 \times). It was dried over sodium sulfate and concentrated in vacuo to get the crude product as crystalline yellow solids. It was purified by column chromatography (silica gel) using hexane–EtOAc/9:1 as eluent. A chromatographic fraction corresponding to $R_f = 0.7$ on TLC (SiO₂, hexane–EtOAc/9:1 as eluent) was isolated to afford 7- α -bromoacetyl-9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene **6** as yellow viscous oil in 75% yield (2.9 g). Spectroscopic data of **6**: FAB⁺–MS calcd for ¹²C₄₅¹H₅₆^{79.9}Br₁¹⁴N₁¹⁶O₁ m/z 706; found, m/z 705 and 707; FT-IR (KBr) ν_{\max} 3037 (w), 2966 (s), 2928 (m), 2878 (w), 1674 (s), 1595 (vs), 1491 (s), 1281 (vs), 754 (s), and 698 (s) cm⁻¹; UV-vis (CHCl₃, 2.0 $\times 10^{-5}$ M) λ_{\max} (ϵ) 299 (3.4 $\times 10^4$) and 407 nm (3.8 $\times 10^4$ L/mol-cm); ¹H NMR (500 MHz, CDCl₃, ppm) δ 7.94 (m, 2H), 7.63 (d, $J = 8$ Hz, 1H), 7.58 (d, $J = 8$ Hz, 1H), 7.27–6.97 (m, 12H), 4.46 (t, $J = 4$ Hz, 2H), 2.08–1.79 (m, 4H), and 1.31–0.39 (m, 34H); ¹³C NMR (500 MHz, CDCl₃, ppm) δ 190.9, 153.4, 150.8, 148.8, 147.6, 146.9, 134.1, 131.5, 129.2, 128.7, 124.3, 124.3, 123.0, 123.0, 122.9, 121.6, 118.8, 118.0, 55.0, 50.8, 50.7, 37.6, 33.0, 32.9, 31.5, 30.9, 29.8, 29.3, 29.3, 22.4, and 22.4.

Synthesis of 7-(1,2-dihydro-1,2-methanofullerene[60]-61-carbonyl)-9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene, the monoadduct C₆₀(>DPAF-C₉) 1. C₆₀ (1.0 g, 1.38 mmol) and 7-bromoacetyl-9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene **6** (970 mg, 1.38 mmol) were dissolved in toluene (700 mL) under an atmospheric pressure of nitrogen. To this was added 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.2 mL, 1.38 mmol) and stirred at room temperature for a period of 5.0 h. At the end of stirring, suspending solids of the reaction mixture were filtered off and the filtrate was concentrated to a 10% volume. Methanol (100 mL) was then added to cause precipitation of the crude product, which was isolated by centrifugation. The isolated solid was a mixture of the monoadduct **1** and bisadduct **2**. Separation of **1** and **2** were made by column chromatography on silica gel using a solvent mixture of

hexane–toluene/3:2 as eluent. The first chromatographic band at $R_f = 0.45$ on the thin-layer chromatographic (TLC, SiO₂) plate using hexane–toluene/3:2 as eluent afford C₆₀(>DPAF-C₉) **1**, as greenish brown solids (960 mg, 70% based on recovered C₆₀). Spectroscopic data of **1**: FAB⁺–MS calcd for ¹²C₁₀₅¹H₅₅¹⁴N¹⁶O m/z 1345.4; found, m/z 1345 and 1346; MALDI–MS (TOF) found, m/z 1349, 1348, 1347, 1346 (MH⁺), 894, 877, 862, 855, 845, 840, 802, 704, 687, 683, 672, 665, 650, 631, 629, 612, and 585; Anal. Calcd for C₁₀₅H₅₅NO: C, 93.68; H, 4.08; N, 1.04; found: C, 93.52; H, 3.88; N, 0.95; UV-vis (CHCl₃, 2.0 × 10⁻⁵ M) λ_{\max} (ϵ) 263 (1.7 × 10⁵), 326 (5.7 × 10⁴), and 410 nm (4.4 × 10⁴ L/mol-cm); FT-IR (KBr) ν_{\max} 3435 (br), 2947 (s), 2922, 2861 (m), 1678, 1593 (vs), 1491 (s), 1464, 1426, 1402, 1347 (w), 1274 (s), 1199 (s), 1185, 1155 (w), 1028 (w), 816 (w), 752 (s), 695 (s), 576, and 526 (vs) cm⁻¹; ¹H NMR (500 MHz, CDCl₃, ppm) δ 8.47 (d, $J = 8.0$ Hz, 1H), 8.33 (s, 1H), 7.82 (d, $J = 8.0$ Hz, 1H), 7.65 (d, $J = 8.0$ Hz, 1H), 7.26 (m, 6H), 7.13 (m, 4H), 7.05 (m, 2H), 5.67 (t, $J = 4.0$ Hz, 1H), 2.1–1.9 (m, 4H), 1.3–1.1 (m, 4H), and 0.9–0.6 (m, 30H); ¹³C NMR (500 MHz, CDCl₃, ppm) δ 189.3, 153.7, 151.4, 149.1, 148.2, 148.20, 147.6, 147.6, 146.9, 145.6, 145.4, 145.3, 145.1, 145.0, 144.9, 144.7, 144.6, 144.6, 144.5, 143.9, 143.7, 143.3, 143.1, 143.1, 143.0, 142.9, 142.9, 142.8, 142.5, 142.2, 142.1, 141.2, 140.9, 139.6, 136.6, 134.0, 133.5, 129.4, 128.9, 124.5, 123.2, 122.8, 121.8, 119.3, 118.0, 72.6, 55.2, 50.9, 44.6, 38.2, 33.2, 30.9, 30.0, 29.5, and 22.6.

Material Characterization

Spectroscopic Data of Monoadduct C₆₀(>DPAF-C₉)₂ **1**.

The molecular ion mass of **1** was clearly detected in positive ion fast atom bombardment mass spectrum (FAB⁺–MS, Figure S2) at m/z 1345/1346 (M⁺/MH⁺). That clearly provides evidence of the composition mass of fullerene-fluorene dyad **1**. In a separate measurement, the molecular ion mass of bisadduct **2** was detected in FAB⁺–MS at m/z 1971 (M⁺). The next major group of mass fragmentation peaks occurred at m/z 720/721 corresponding to the ion mass of the C₆₀ cage. The relatively simple spectrum in the higher mass region revealed high stability of aromatic diphenylaminofluorene moiety under FAB⁺–MS measurement conditions. That led to the bond cleavage occurring only at the cyclopropanyl carbon conjunction bonds bridging fullerene and DPAF moieties.

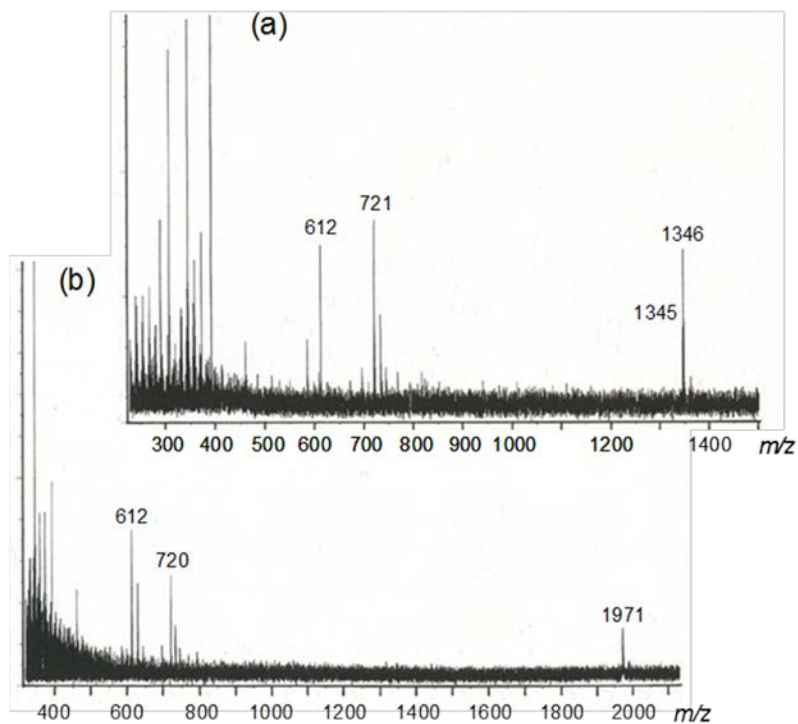


Figure S2. Positive ion FAB mass spectrum (direct probe) of (a) $C_{60}(>DPAF-C_9)$ **1** and (b) $C_{60}(>DPAF-C_9)_2$, showing the corresponding molecular ion mass at m/z 1345 and 1971, respectively, for confirmation of their molecular mass.

We assigned all proton peaks in 1H NMR spectrum of **1**. The α -proton (H_a next to the carbonyl group) peak of **1** appeared as a triplet at δ 5.69 (Fig. S3a) with a large downfield shift of roughly 1.2 ppm from that of **6**. It was also accompanied with downfield shift of all phenyl proton at C5, C6, and C8 of the fluorene moiety to 7.83 (d, $J = 8$ Hz), 8.48 (d, $J = 8$ Hz), and 8.34 (s). In the case of the bisadducts $C_{60}(>DPAF-C_9)_2$, comparable 1H NMR spectra were obtained. For example, using the spectrum of **1** as the reference, we assigned the multiplet peaks at δ 7.7–7.9 (2H), 8.2–8.35 (2H), and 8.35–8.6 (2H) in Fig. S3b for the chemical shift of H_5 , H_8 , and H_6 protons, respectively. There are two groups of proton peaks at δ 5.35–5.6 and 5.6–5.85 in a different integration intensity accounted for a total of two types of α -protons each with both H_a and H_b in a slightly different chemical shift value. That revealed only two possible regioisomers of the bisadduct in a molecular ratio of roughly 1:2.8 in the isolated, chromatographically non-separable fraction, as a result of the large DPAF moiety size and a close similarity of the molecular polarity between these two regioisomers.

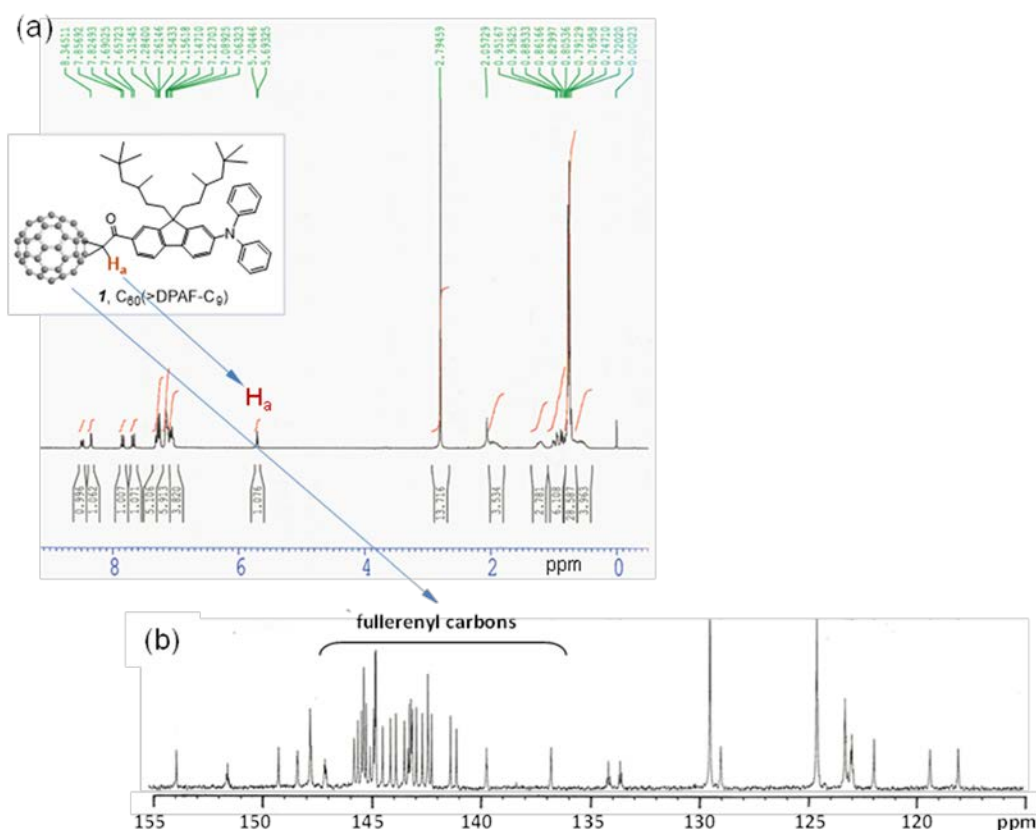


Figure S3. (a) ¹H and (b) ¹³C NMR spectra of the monoadduct C₆₀(>DPAF-C₉) **1** indicating a C₂ molecular symmetry with a total of 29 fullerenyl *sp*² carbons.

By using DEPT (Distortionless Enhancement by Polarization Transfer) measurement of ¹³C NMR spectrum of C₆₀(>DPAF-C₂) as a reference to assist identification of carbon groups in the structures of **1**. We were able to differentiate the carbon chemical shift of C9 and fullerenyl *sp*³ carbons to be δ 55.2 and 72.6, respectively. The chemical shift of cyclopropanyl carbon next to the keto group was found to be δ 44.6. The most downfield peak at δ 189.3 was assigned to the bridging carbonyl carbon. All other fullerenyl carbons appeared as a total of 29 peaks in the region of δ 136 to 147 accounted for 58 *sp*² carbons of the fullerene cage (Fig. S3c), indicating clearly a C₂ symmetry axis along the plane of two *sp*³ fullerene carbons that provides the confirmation of a molecular symmetry for dyad **1**.

Back-light Illuminating Monostatic RF Measurement Setup

