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ChemComm www.rsc.org/chemcomm

Synthesis of C_{60}-diphenylaminofluorene dyad with large 2PA cross-sections and efficient intramolecular two-photon energy transfer

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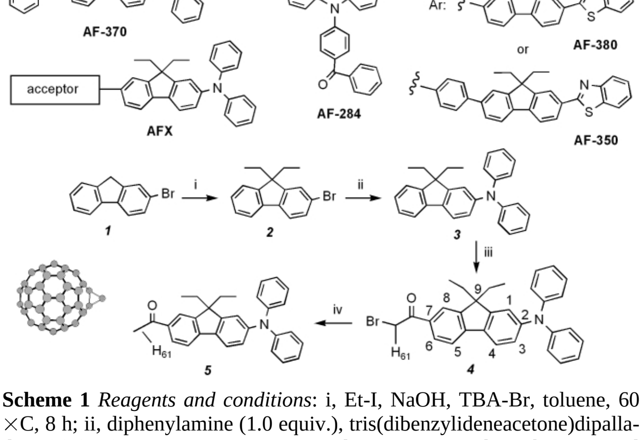
Received (in Cambridge, UK) 20th March 2002, Accepted 6th June 2002
First published as an Advance Article on the web 24th July 2002

The first, highly two-photon active C_{60} derivative comprised of a A-sp^3-D conjugate structure was synthesized showing effective two-photon absorption cross-sections ($\sigma_2{}' = 196 \times 10^{-48}$ cm^4 sec^{-1} molecule^{-1}) in the nanosecond regime among the best values for diphenylaminofluorene-based AFX chromophores.

The concept of multi-dimensional conjugation and dendrimer structure as an approach for enhancing the cross-sections of 2PA molecules was recently demonstrated.[1–3] As the first step toward new multidimensional conjugated 2PA chromophores, we prepared, to our best knowledge, the *first*, highly two-photon active C_{60} derivative possessing a one-dimensional A-sp^3-D conjugate system with coupling of the electron-accepting (A) fullerene cage and the electron-donating (D) diphenylaminofluorene (DPAF).

Synthesis of C_{60}-diethyl-2-diphenylaminofluorene dyad was made using ketomethane as a linker analogous to the mono-functionalized C_{60} malonate derivative forming a cyclopropane moiety at the [6,6]-bond, as demonstrated by Bingel.[4] The resulting phenylketone structure may allow better carbonyl interaction with π-orbitals of the C_{60} cage with a higher density of π-electrons at a close vicinity than the corresponding methano[60]fullerene malonate esters. As the phenyl ring is being replaced by a larger conjugated chromophore, the partial extended π-electron interaction through space with the C_{60} cage may be enhanced despite a small steric gap of the sp^3 carbon in between. Accordingly, diethyl-2-diphenylaminofluorene **3** was synthesized in a yield of 98% by the reaction of 2-bromo-9,9-diethylfluorene **2** with diphenylamine (1.0 equiv.) under catalytic condensation conditions in refluxing toluene in the presence of tris(dibenzylideneacetone)dipalladium(0) catalyst (0.25 mmol%), *rac*-BINAP ligand (0.75 mmol%), and sodium *tert*-butoxide (1.5 equiv.).[5] Compound **2** was prepared from 2-bromofluorene **1**, iodoethane, and NaOH in toluene using tetrabutylammonium bromide as a phase transfer catalyst (Scheme 1).[6] Friedel–Crafts condensation of **3** with a mixture of bromoacetyl bromide and aluminium chloride in 1,2-dichloroethane at 0–10 °C afforded 7-bromoacetyl-9,9-diethyl-2-diphenylaminofluorene **4** ($R_f = 0.3$, SiO_2, hexane : toluene 3 : 2, m/z 510 as shown in the negative ion DCI-MS) as a yellow crystalline solid in 66% yield. The chemical shift of the α-proton (H_{61}) was found to be δ 4.49 in the ^1H NMR spectrum ($CDCl_3$, 400 MHz). Assignment of the bromoacetyl group attachment on the C_7 atom of diphenylaminofluorene **4** was made by the down-field shift of phenyl protons at C_5, C_6, and C_8 to δ 7.65 (d, J = 7.8 Hz), 7.95 (dd, J = 7.8 and 1.4 Hz), and 7.93 (d, J = 1.4 Hz), respectively. It was also confirmed by the crystal structure of the final product **5**. The reaction of C_{60} with **4** (1.0 equiv.) in toluene using DBU (1.0 equiv.) as a base at ambient temperature for a period of 5 h, followed by partial solvent removal and the subsequent work-up gave 7-(1,2-methano[60]fullerene-61-carbonyl)-9,9-diethyl-2-diphenylaminofluorene **5** ($R_f = 0.6$, SiO_2, hexane : toluene 3 : 2) as a greenish brown solid in 52% yield (or 71% based on recovered C_{60}). A clear large down-field shift of the α-proton (H_{61}) peak with more than 1.2 ppm to δ 5.70 was observed in the ^1H NMR spectrum ($CDCl_3$, 400 MHz). It was also accompanied with down-field shifts of all phenyl proton peaks at C_5, C_6, and C_8 to δ 7.83 (d, J = 8.0 Hz), 8.48 (dd, J = 8.0 and 1.3 Hz), and 8.32 (d, J = 1.3 Hz), respectively. The corresponding shifts were 0.18, 0.53, and 0.39 ppm. Interestingly, the value of the δ shift is reverse proportional to the distance between the proton affected and the fullerene cage with a larger value for $H_{61} > H_6 > H_8 > H_5$. It can be correlated to de-shielding of these protons by the fullerene ring currents indicating active interactions occurring between C_{60} and the 2PA-active fluorene.

Single crystals of **5** were successfully obtained from CS_2–EtOH by a slow diffusion method in a H-tube. The X-ray structural analysis of this crystal† gave verification of the molecular structure and indicated a monoclinic unit cell with a space group of $P2_1/n$ and dimensions of a = 10.00 Å, b = 19.58 Å, c = 25.72 Å, $\alpha = 90°$, $\beta = 93.05°$, and $\gamma = 90°$ with final residues of the refinement [$I > 2\sigma(I)$] $R_1 = 0.052$ and $wR_2 = 0.128$. The unit cell packing structure is shown in Fig. 1. The molecular packing of **5** is apparently dominated by the fullerene moieties with a tightly ordered assembly in close contact, indicating a strong hydrophobic interaction between C_{60} cages. All fluorene moieties are scattered around fullerene surroundings showing no direct intermolecular flourene–fluorene-overlapping. Accordingly, similar behavior of the molecular assembly may be expected in solids or the solution in a high



Scheme 1 *Reagents and conditions*: i, Et-I, NaOH, TBA-Br, toluene, 60 ×C, 8 h; ii, diphenylamine (1.0 equiv.), tris(dibenzylideneacetone)dipalladium(0) (cat.), *rac*-BINAP, *t*-BuONa, toluene, 110 °C, 8 h; iii, bromoacetyl bromide, $AlCl_3$, CH_2CH_2, 0 °C to rt, 4 h; iv, C_{60}, DBU, toluene, rt, 5 h.

DOI: 10.1039/b202681c

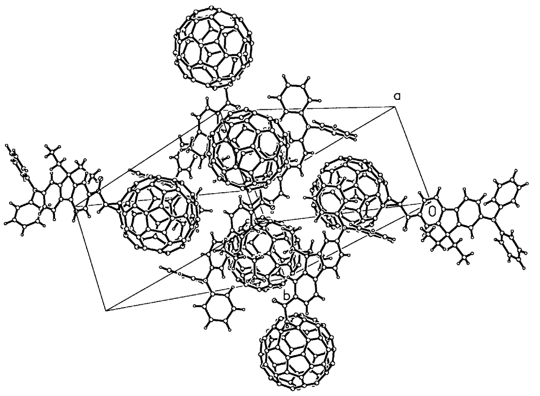


Fig. 1 Unit cell packing structure of **5** showing a well-organized assembly of fullerene cages with scattered diethyldiphenylaminofluorene moieties.

concentration, which was used in the 2PA absorption measurements. Solubility of DPAF moieties in CS_2 and ODCB is high. As the concentration of **5** in CS_2 increases, we propose that strong interaction and possible aggregation of fullerene cages should lead to formation of nano-clusters with DPAF segments dispersed in CS_2.

Effective 2PA cross-section values of **5**, AF-350, AF-284, and AF-370 in a solution concentration of 0.02 M were obtained by measuring the nonlinear transmissivity of a given sample as a function of the intensity of the input laser beam. The beam was provided by a pulsed tunable dye laser working at ~800 nm wavelength, ~8 ns pulse duration, and 10 Hz repetition rate. An optical path-length of 1.0 cm was applied. The technical details of 2PA measurements in the nanosecond regime were described elsewhere.[7] Molecular two-photon absorption cross-sections (σ_2 in an unit of $cm^4\ GW^{-1}\ molecule^{-1}$) were obtained from the nonlinear absorption coefficient β of the sample. Interestingly, the effective molecular 2PA cross-section ($\sigma_2' = h\upsilon\sigma_2$) of **5** in CS_2 under a linearly polarized 800 nm pulsed beam was found to be 196 $\times 10^{-48}$ $cm^4\ sec^{-1}\ molecule^{-1}$, which is among the highest 2PA cross-section values obtained for many chromophores of the AF series to date.

The comparison of optical properties of **5** with several good 2PA chromophores at 800 nm pumping was summarized in Table 1. For the consistency in comparison of materials optical properties, all samples were measured under similar conditions. Apparently, 2PA characteristics of the linear A-sp^3-D conjugate **5** in the nanosecond regime are nearly double in the cross-sections of its parent linear analogue AF-370 and in the same range as that of the quadrupolar analogue AF-284. The value is only less than 30% lower than σ_2' (278×10^{-48} $cm^4\ sec^{-1}\ molecule^{-1}$) of the 2PA benchmark for AFX series, namely, the octupolar analogue AF-350. Since the number density is a significant factor in enhancing the 2PA cross-sections, the fullerene cage should serve well as a nucleus center of the fluorene dye in increasing the dimensionality. Furthermore, this result also suggests that C_{60} with multiple AFX branches may lead to similar cooperative interactions reported for a three-armed oxadiazole–triarylamine system[1] similar to AF-350 and AF-380. It should be noted that the effective 2PA cross-section value measured for **5** may involve the contribution from excited-state absorption of the C_{60} cage and a reverse saturable absorption occurring in tandem with the 2PA process similar to the proposed sequence of intersystem crossing and excited state absorption processes in the blend of AF-380 and C_{60}.[8]

Table 1 2PA optical properties of chromophores at 800 nm pumping

Chromophore	λ_{max}/nm[a]	λ_{max}/nm[b] emission	$\sigma_2/\times 10^{-20}$ $cm^4\ GW^{-1}$ molecule^{-1c}	$\sigma_2'/\times 10^{-48}$ $cm^4 sec^{-1}$ molecule^{-1c}
AF-350/THF	400	485	112	278
5/CS_2	408	None	79	196
AF-284/THF	403	480	79	196
AF-370/THF	389	484	42	104

[a] Linear absorption of the fluorene unit. [b] Under an excitation wavelength of 380 nm. [c] At a concentration of 0.02 M under a pumping wavelength of 800 nm, uncertainty of cross-section measurement: ±15%.

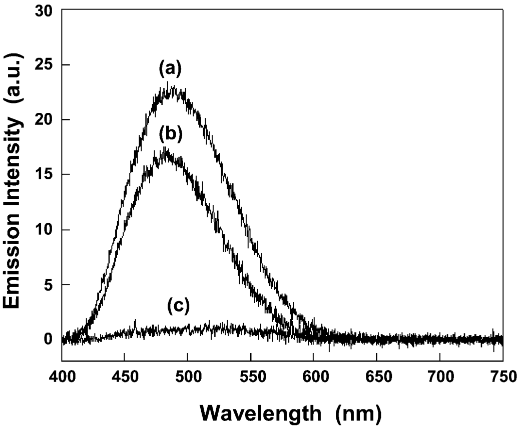


Fig. 2 Relative 2PA-induced emission intensity of (a) AF-284 in THF (1.0×10^6 M), (b) AF-370 in THF (1.0×10^6 M), and (c) **5** in CS_2 (1.0×10^4 M) upon photoexcitation at 800 nm using a pulsed tunable dye laser.

Finally, only a low 2PA-induced emission intensity was observed in **5** (CS_2, 1.0×10^{-4} M, Fig. 2c) upon pulse laser excitation at 800 nm. Whereas a relatively high contrast in intensity of the 2PA-induced emission can be detected at λ_{max} 480 and 484 nm for the samples of AF-284 and AF-370, respectively, as shown in Figs. 2a and 2b, even in a low concentration of 1.0×10^{-6} M. The phenomena were interpreted as an effective *intramolecular* energy transfer, after two-photon absorption, from the diethyldiphenylaminofluorene moiety to the fullerene cage as evidenced by the complete quenching of fluorescence normally observed for AFX chromophores. A similar quenching effect due to the energy transfer upon linear photoexcitation of chromophore-C_{60} dyads was also reported, in addition to a possible electron transfer mechanism.[9]

The work was partially supported by AOARD/Airforce Office of Scientific Research.

Notes and references

† *Crystal data* of **5**: $C_{91}H_{27}NO$, 1150.14 (*M*), monoclinic, $P2_1/n$, $T = 295$ (2) K, $a = 10.00100$ (10) Å, $b = 19.5790$ (2) Å, $c = 25.7150$ (3) Å, $\alpha = 90°$, $\beta = 93.0510$ (10)°, $\gamma = 90°$, $V = 5028.11$ (9) Å^3, $Z = 4$, $R_{int} = 0.0396$, abs. coefficient 0.089 mm^{-1}, $R_1 = 0.0524$ and $wR_2 = 0.1279$ for $I > 2\sigma$ (*I*). CCDC 183726. See http://www.rsc.org/suppdata/cc/b2/b202681c/ for electronic files in .cif or other electronic format.

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