The impact of charge defects and resonance enhancement on the two-photon absorption activity of spirofluorene and ladder-type pentaphenylene derivatives

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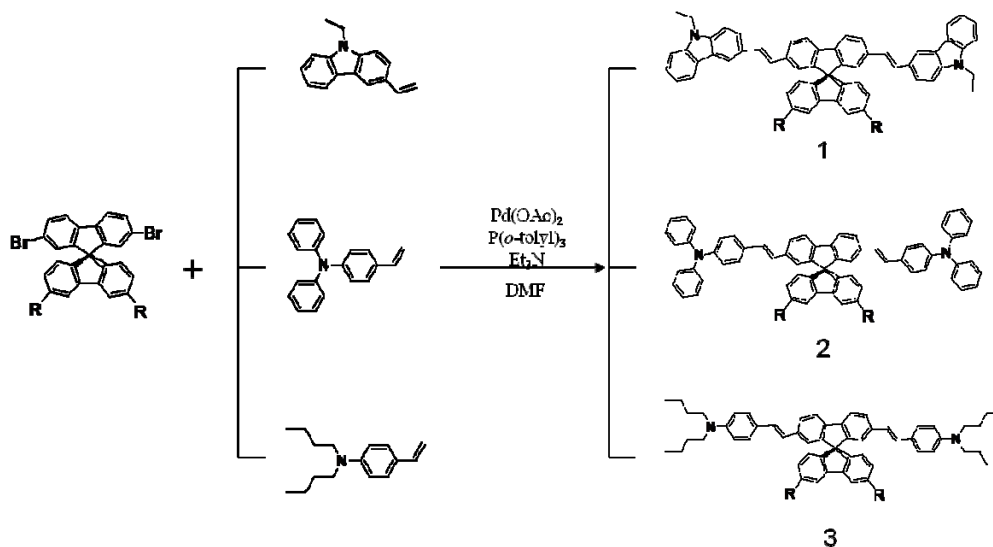   (AIST), AIST Kansai Center, Ikeda, Osaka 563-8577, Japan
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1. Synthesis

Scheme S1. Synthetic procedure of compounds 1-3.

9-Ethylcarbazole, triphenylamine, and *N,N*-di-*n*-butylaniline, obtained from Aldrich Chemical Corporation, were used without any further purification. Compounds 1-3 were formylated via the Vilsmeier reaction, and then, formyl groups of these compounds were converted into vinyl groups through the Wittig coupling reaction.[S1] Vinyl-substituted 9-ethylcarbazole, triphenylamine, and *N,N*-dibutylaniline were coupled with 2',7'-dibromo-3,6-bis(3,7-dimethyloctyloxy)-9,9'-spirobifluorene using the Heck coupling reaction to obtain compounds 1–3[S2]. The detailed synthetic methods are described below.

Compound 1: 2',7'-Dibromo-3,6-bis(3,7-dimethyloctyloxy)-9,9'-spirobifluorene (0.1 g, 0.127 mmol), 9-ethyl-3-vinyl-9*H*-carbazole (67 mg, 0.305 mmol), palladium acetate (1.7 mg, 0.00762 mmol), tri-*o*-tolylphosphine (2.3 mg, 0.00762 mmol), and tributylamine (5 mL) in *N,N*-dimethylformamide (DMF) (5 mL) were refluxed for 24 h. The solvent was removed and the mixture was poured into methanol. The precipitate was purified by flash column chromatography using *n*-hexane/methylene chloride (4:1 in vol.) as eluent. The product was recrystallized, and then, compound 1 was collected by filtration as a yellow solid (54% yield) with a melting point (m.p.) of 168-170°C.

^{1}H NMR (300 MHz, CDCl$_3$, 25 $^{\circ}$C, TMS): δ=8.13 (2H, s), 8.08 (2H, d, J=8.52 Hz), 7.81 (2H, d, J=7.69), 7.57 (4H, t), 7.51–6.93 (16H, m), 6.73 (4H, s), 4.35 (4H, q), 4.11 (4H, t), 1.89 (2H, m)), 1.78-1.11 (22H, m), 0.99 (6H, d, J=6.32)), 0.89 (12H, d, J=6.04); ^{13}C NMR (300 MHz, CDCl3, 25 $^{\circ}$C, TMS) : δ=13.92, 19.81, 22.72, 24.76, 28.06, 29.95, 36.44, 37.38, 37.63, 39.33, 64.65, 66.56, 105.78, 108.48, 114.37, 118.56, 118.86, 119.93, 120.32, 121.29, 122.84, 123.08, 124.18, 124.81, 125.81, 128.46, 129.00, 137.44, 139.48, 140.14, 141.42, 142.94, 150.04, 159.27; MS (EI): *m/z* 1067.64 (M+1)$^{+}$; Anal. Calcd for C$_{77}$H$_{82}$N$_2$O$_2$: C, 86.64, H, 7.74, N, 2.62, O, 3.00. Found: C, 86.07, H, 7.73, N, 2.56, O, 3.65.

Compound 2: The synthetic procedure for compound **2** and its characterizations are described elsewhere.[S3]

Compound 3: 2',7'-Dibromo-3,6-bis(3,7-dimethyloctyloxy)-9,9'-spirobifluorene (0.1 g, 0.127 mmol), dibutyl(4-vinyl-phenyl)amine (71 mg, 0.305 mmol), palladium acetate (1.7 mg, 0.00762 mmol), tri-*o*-tolylphosphine (2.3 mg, 0.00762 mmol), and tributylamine (5 mL) in DMF (5 mL) were refluxed for 24 h. The solvent was removed, and the mixture was poured into methanol. The precipitate was purified by column chromatography using *n*-hexane/methylene chloride (4:1 in vol.) as eluent. The product was recrystallized, and then, compound **3** was collected by filtration as a yellow solid (45% yield) with a m.p. of 111-113ºC.

^{1}H NMR (300 MHz, CDCl$_3$, 25 ºC, TMS): δ=7.73 (2H, d, *J*=7.69), 7.45 (2H, d, *J*=7.69 Hz), 7.38 (2H, t), 7.25 (4H, m), 6.88 (2H, s), 6.83 (2H, s), 6.75 (2H, s), 6.7 (4H, s), 6.56 (4H, d, *J*=8.24), 4.09 (4H, t), 3.26 (8H, t), 1.87 (4H, m), 1.78-1.13 (38H, m), 1.04-0.78 (24H, m); ^{13}C NMR (300 MHz, CDCl$_3$, 25 ºC, TMS): δ= empty space for ^{13}C NMR; MS (EI): *m/z* 1087.80 (M+1)$^+$; Anal. Calcd for C$_{77}$H$_{102}$N$_2$O$_2$: C, 85.03, H, 9.45, N, 2.58, O, 2.94. Found: C, 82.63, H, 9.56, N, 2.40, O, 3.13.

Compounds 4–6: The synthetic procedures for compounds **4–6** and their characterization are described elsewhere.[S4]

2. Measurements

Spectroscopic Measurements: UV/Vis absorption spectra were recorded on a Shimadzu 310pc spectrophotometer in a THF solution (1x10^{-5} M for all compounds). The transition dipole moment M_{ge} (in Debye units) can be obtained by integrating the absorption band (Equation 3)[S5]:

$$M_{ge} = \left[\frac{1}{nf(n)} \frac{2303}{8\pi} \frac{3hc}{N_A} \int \frac{\varepsilon(v)}{v} dv \right]^{\frac{1}{2}} = 9.584 \times 10^{-2} \left[\frac{1}{nf(n)} \int \frac{\varepsilon(v)}{v} dv \right]^{\frac{1}{2}} \tag{3}$$

where N_A is Avogadro's number, $\varepsilon(v)$ is the extinction coefficient, h is the Planck constant, c is the speed of light, v is the optical frequency (in wavenumber), and n is the refractive index of the solvent. Fluorescence spectra were obtained using a Horiba/Jobin-Yvon spectrofluorometer (SPEX 270M). The fluorescence quantum yield (Φ_f) were determined by comparison with a Coumarin 102 (Aldrich, 99%, $\Phi_f = 0.93$ in ethanol) as a reference according to the following equation (4):

$$\Phi_x = \Phi_{st}(slope_x/slope_{st})(n^2_x/n^2_{st}) \tag{4}$$

where Φ is the quantum yield, slope is the slope from the plot of integrated fluorescence intensity versus absorbance at the excitation wavelength, and n is the refractive index of the solvent. The subscripts x and st refer to an unknown and standard sample, respectively.[S6] Fluorescence lifetimes were measured by time-correlated single-photon counting (TCSPC).

Two-photon absorption measurement: TPA spectra were obtained by two different methods: The first one was the two-photon-induced fluorescence (TPIF) method using a femtosecond Ti:Sapphire laser (Spectra Physics *Tsunami*) with a pulse duration of about 100 fs operating at a repetition rate of 82 MHz in the 700–900 nm spectral region. The optical setup for these experiments has been described previously.[S7] Coumarin 307 in methanol (10^{-4} M) and fluorescein in water (pH 11) were used as references.[S8] The second method was the open-aperture Z-scan method using a femtosecond optical parametric amplifier (Spectra Physics *OPA-800)* pumped by a Ti:Sapphire regenerative amplifier system (Spectra Physics *Spitfire)* with a pulse duration of typically 130 fs operating at repetition rate of 1 kHz in the 600–1000 nm spectral region. For each measurement, we examined the effect of the incident power on the nonlinear absorption signal of the Z-scan traces at four or more different powers below 0.3 mW to check the observed nonlinear processes originating from the simultaneous

TPA process. The sample solution was held in a quartz cuvette with an optical path length of 1 mm (shorter than the Rayleigh range of the optical setup, which is 4 mm or longer) to keep the "optically thin" conditions during all the measurements. These conditions gave an on-axis peak intensity below 140 GW/cm^2 at the focal position. The TPA coefficient and TPA cross-section were calculated by curve fitting of the model function assuming a spatial and temporal Gaussian pulse for the recorded Z-scan traces. Further details on the optical setup and the data-processing procedure have been described previously.[S9,S10]

3. Geometry Optimization:

The molecular geometries were optimized using the semi-empirical method Austin Model 1 (AM1) level impanted in Gaussian, and the molecular structures were simplified by replacing the long alkyl chains and side aryl moieties with methyl groups (as displayed in Fig. 3). The electronic structure of the compounds in the ground state was calculated using a semi-empirical intermediate neglect of a differential overlap (INDO) Hamiltonian, coupled to a multi-reference determinant single and double configuration–interaction (CI) technique (INDO/MRD-CI).[S11] The Mataga–Nishimoto (MN) potential was used to describe the Coulomb-repulsion terms.

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