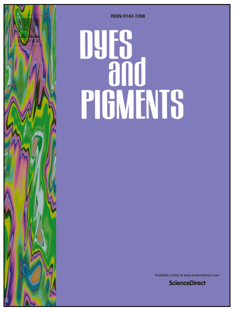

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Substituent effect on quantum efficiency in 4-aryloxy-*N*-(2’,6’-diisopropylphenyl)-1,8-naphthalimides: Experimental and computational investigations

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Abstract

A series of potential optical brightening agents - 4-aryloxy-*N*-(2’,6’-diisopropylphenyl)-1,8-naphthalimides - are synthesized and their photo-physical properties are experimentally determined. Interestingly, it is found that their quantum efficiencies or quantum yields are exclusively dependent on the substituents on the aryloxy group at the 4-position. It is postulated that the electronic effect of the substituents influences the photo-induced electron transfer process, which causes a variation in quantum efficiencies. Due to analysis of charge transfer from 1,8-naphthalimide molecular part to its substituents in dichloromethane based on the time-dependent density functional theory at Becke 3-parameters Lee-Yang-Parr level coupling with the 6-31G(d) basis set in the conductor-like polarizable continuum model with the united atom topological model computations, it is found that computed charge transfers of these serial compounds correspond well with their experimental quantum yields. Validation of the calculation method is performed by experimental determination of the quantum yield of the nitro-substituted compound.

Keywords:

N-Aryl naphthalimide

Quantum yield

Optical brightener

Photo-induced electron transfer

TDDFT

1. Introduction

With their good photo- and thermo stabilities, 1,8-naphthalimide derivatives have been used as optical brighteners (OB) or fluorescent brightening agents (FBA) [1] - compounds that can improve whiteness of other materials or surfaces by compensating the blue defects with their blue fluorescent light [2]. Several derivatives of 1,8-naphthalimides with noble fluorescence property have also been applied as signal transducers in fluorescent chemosensors [3] and materials in optoelectronic devices [4]. In our research on synthesis and study of fluorescent compounds, we became interested in the 4-substituted-1,8-naphthalimide derivatives due to their generally high emission quantum efficiencies. We herein reported our synthesis and photophysical properties of a series of *N*-aryl-4-aryloxy-1,8-naphthalimide. The quantum efficiencies of these compounds depend on the electronic property of the aryloxyl moiety at the 4-position which can be related to photo induced electron transfer (PET) process. The density functional theory (DFT) and time-dependent density functional theory (TDDFT) calculations [5,6] yielded a linear relationship between the fluorescence quantum efficiency and the degree of charge transfer which is useful for the quantum efficiency prediction.

2. Experimental

2.1 Chemicals and instruments

4-Bromo-1,8-naphthalic anhydride, 4-methoxyphenol, 4-tert-butylphenol, 4-chlorophenol, methyl 4-hydroxybenzoate, 4-cumylphenol, and 2,6-diisopropyl aniline were purchased from Sigma-Aldrich (USA) and used without purification. Phenol, 1-butanol, potassium hydroxide, and potassium carbonate were purchased from Fluka (Switzerland) and used without purification. Acetic acid and DMF were reagent grade purchased from Aldrich (USA). They were stored over 4Å molecular sieve with N_2 bubbling for 1 h prior to use. Commercial *n*-hexane, ethyl acetate and methanol were fractionally distilled before use.

The ^{1}H NMR experiments were preformed on a Varian Mercury NMR spectrophotometer (Varian, USA) at 400 MHz with chemical shifts reported as ppm in $CDCl_3$. The ^{13}C NMR was measured on Bruker Mercury NMR spectrophotometer (Bruker, Germany) which equipped at 100 MHz with chemical shifts reported as ppm in $CDCl_3$. A UV-2550 UV-visible spectrophotometer (SHIMADZU, Japan) was used for the absorption studies. Emission spectra were acquired by a Carry Eclipse Fluorescence Spectrophotometer (Agilent Technologies). Fluorescent lifetimes were measured by a Horiba Jobin Yvon FluoroMax 4 (Horiba Jobin Yvon, France) using the time correlated single photon counting method with the following settings: excitation source, 370 nm NanoLED; time range, 100 ns; peak preset 10,000 counts; repetition rate at 1 MHz; coaxial delay of 60ns. Cyclic voltammograms were obtained from an Autolab voltammetry instrument.

2.2 Synthesis

4-bromo-N-(2’,6’-diisopropylphenyl)-1,8-naphthalimide (**2**)

4-Bromo-1,8-naphthalic anhydride (**1**) (1.0 g, 1.07 mmol) and 6 mL glacial acetic acid were added into a round bottom flask, then 2,6-diisopropylaniline (0.33 mL, 0.31 g, 1.75 mmol) was added and the mixture was heated under refluxing conditions for 12 h. After the reaction was allowed to cool to room temperature, the mixture was poured into 30 g of ice and the resulting precipitate was filtered, washed with cool water, and dried over a steam bath. The white powder was purified by column chromatography that used hexane/ethyl acetate (10:1) as the eluent to obtain **2** as white crystalline solid (81%). ^{1}H NMR ($CDCl_3$) δ (ppm): 1.05 (d, 12H), 2.65 (m, 2H), 7.25 (d, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.85 (t, *J* = 7.8 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 8.40 (d, *J* = 8.0 Hz, 1H), 8.59 (d, *J* = 7.6 Hz, 1H), 8.66 (d, *J* = 7.2 Hz, 1H). These NMR data are in accordance with the literature information [7].

General procedure of 4-aryloxy-*N*-(2’,6’-diisopropylphenyl)-1,8-naphthalimide (A-G)

To a mixture of **2** (0.11 g, 0.25 mmol), anhydrous K_2CO_3 (0.10 g, 0.75 mmol), and DMF (6 mL), 2 mole equivalent of a phenolic compound was added and the reaction was heated at 110 ^oC and stirred for 12 h. The mixture was then poured into ice/water and the crude precipitate was collected by vacuum filtration and washed with water. Target compound was obtained after purification by column chromatography using hexane/ethyl acetate (10:1) as the eluent.

4-(4-Methoxy-phenoxy)-N-(2’,6’-diisopropylphenyl)-1,8-naphthalimide (**A**)

This compound was synthesized from **2** and 4-methoxyphenol in 81% yield. ^1H NMR ($CDCl_3$) δ (ppm): 1.15 (m, 12H), 2.74 (m, 2H), 3.88 (s, 3H), 6.90 (d, *J* = 8.4 Hz, 1H), 7.00 (d, *J* = 9.2 Hz, 2H), 7.15 (d, *J* = 9.2 Hz, 2H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.83 (t, *J* = 8.4 Hz, 1H), 8.50 (d, *J* = 8.4 Hz, 1H), 8.70 (d, *J* = 8.4 Hz, 1H), 8.80 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ (ppm): 24.0, 29.1, 55.7, 109.8, 115.5, 116.2, 122.0, 122.7, 123.9, 126.5, 128.9, 129.4, 130.4, 131.1, 132.4, 133.4, 145.7, 147.9, 157.4, 161.0, 163.8, 164.4.

4-(4-tert-Butyl-phenoxy)-N-(2’,6’-diisopropylphenyl)-1,8-naphthalimide (**B**)

This compound was synthesized from **2** and 4-tert-butylphenol in 78% yield. ^1H NMR ($CDCl_3$) δ (ppm): 1.16 (d, 12H), 1.39 (s, 9H), 2.75 (m, 2H), 7.00 (d, *J* = 8.4 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.45–7.55 (m, 3H), 7.85 (t, *J* = 8.4 Hz, 1H), 8.52 (d, *J* = 8.4 Hz, 1H), 8.73 (d, *J* = 8.4 Hz, 1H), 8.80 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ (ppm): 24.0, 29.1, 31.5, 34.6, 110.5, 116.4, 120.2, 122.7, 124.0, 124.2, 126.5, 127.3, 128.9, 129.4, 130.4, 131.0, 132.4, 133.4, 133.6, 145.7, 148.7, 152.4, 160.4, 163.8, 164.4.

4-Cumylphenoxy-N-(2',6'-diisopropylphenyl)-1,8-naphthalimide (**C**)

This compound was synthesized from **2** and cumylphenol in 89% yield. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.08 (d, 12H), 1.67 (s, 6H), 2.67 (m, 2H), 6.80 - 7.30 (m, 12H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.75 (t, *J* = 7.8 Hz, 1H), 8.45 (d, *J* = 8.4 Hz, 1H), 8.64 (d, *J* = 7.2 Hz, 1H), 8.70 (d, *J* = 8.4 Hz, 1H), ^{13}C NMR ($CDCl_3$) δ (ppm): 24.0, 29.2, 30.9, 42.9 110.7, 114.8, 120.2, 125.9, 126.8, 128.2, 128.9, 129.4, 132.4, 133.4, 145.8, 148.4, 150.3, 152.6, 160.3, 163.8, 164.5.

4-Phenoxy-N-(2',6'-diisopropylphenyl)-1,8-naphthalimide (**D**)

This compound was synthesized from **2** and phenol in 79% yield. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.20 (d, 12H), 2.80 (m, 2H), 7.00 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 2H), 7.53 (dd, *J* = 6.4 Hz and 7.6 Hz, 2H), 7.85 (t, *J* = 7.6 Hz, 1H), 8.57 (d, *J* = 8.0 Hz, 1H), 8.77 (d, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 8.61 (d, *J* = 8.0 Hz, 1H), 8.67 (d, *J* = 6.8 and 7.6 Hz, 1H), 8.83 (d, *J* = 8.0 Hz, 1H).^{13}C NMR ($CDCl_3$) δ (ppm): 14.2, 24.0, 29.3, 110.9, 115.4, 116.7, 120.8, 122.8, 124.3, 125.7, 126.7, 128.9, 129.5, 130.5, 131.1, 132.5, 133.4, 145.8, 155.0, 160.2, 163.8, 164.5.

4-(4-Chloro-phenoxy)-N-(2',6'-diisopropylphenyl)-1,8-naphthalimide (**E**)

This compound was synthesized from **2** and 4-chlorophenol in 96% yield. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.13 (s, 12H), 2.72 (m, 2H), 6.95 (d, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 3H), 7.84 (t, *J* = 8.0 Hz, 1H), 8.50 (d, *J* = 8.0 Hz, 1H), 8.65 – 8.75 (m, 2H). ^{13}C NMR ($CDCl_3$) δ (ppm): 24.0, 29.1, 111.0, 117.2, 121.9, 122.8, 124.0, 124.2, 126.8, 128.6, 129.4, 130.4, 130.5, 130.9, 132.5, 133.1, 145.7, 153.6, 159.6, 163.6, 164.3.

4-(4-Carbomethoxy-phenoxy)-N-(2',6'-diisopropylphenyl)-1,8-naphthalimide (**F**)

This compound was synthesized from **2** and methyl 4-hydroxybenzoate in 19% yield. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.15 (d, 12H), 2.74 (m, 2H), 3.95 (s, 3H), 7.10 (d, J = 8.4 Hz, 1H), 7.20 (d, J = 8.8 Hz, 2H), 7.33 (d, J = 7.6 Hz, 2H), 7.48 (t, J = 7.6 Hz, 1H), 7.85 (t, J = 8.4 Hz, 1H), 8.15 (d, J = 8.8 Hz, 2H), 8.57 (d, J = 8.4 Hz, 1H), 8.70 (d, J = 8.4 Hz, 1H), 8.74 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ (ppm): 24.0, 29.1, 52.3, 112.8, 117.9, 119.5, 122.9, 124.0, 124.6, 127.0, 128.6, 129.5, 130.4, 130.8, 132.2, 132.6, 133.0, 145.7, 158.5, 159.5, 163.6, 164.2, 166.2.

2.3 Photophysical properties

Absorption

The stock solution of each compound was prepared in CH_2Cl_2 at 10^{-5}–10^{-3}M, then diluted to more than 5 different concentrations. To obtain accurate results, all absorbance should not exceed 1.0. The molar absorptivity (ε) was obtained from the slope of the calibration curve between concentration and absorbance. The λ_{max} was chosen from the wavelength that provides the highest absorbance.

Emission

The emission spectra were obtained with the excitation wavelength at 364 nm using a slit width of 5 nm and the PMT was controlled at 595 volts (for the compound with $\Phi < 0.50$) and at 540 volt (for the compound with $\Phi \geq 0.50$).

Determination of quantum efficiency

The emission quantum efficiency was determined from the slopes of a plot between the fluorescence integral and absorbance at λ_{max} of each compound compared with that of quinine sulfate in 0.1 M H_2SO_4 used as the standard with the quantum efficiency of 0.54. The calculation was corrected by the square of refractive indices according to the reference method [8].

2.4 Electrochemical analysis

For cyclic voltammogram, an electrochemical cell composed of a Ag/ $AgNO_3$ (0.01 M) reference electrode, glassy carbon (working electrode), and Pt wire electrode counter electrode was configured under nitrogen atmosphere. A 0.1 M solution of supporting electrolyte (tetrabutylammonium hexafluorophosphate, $TBAPF_6$) in acetonitrile was used as a solvent for the preparation of 1 mM solution of tested compounds. All cyclic voltammograms were recorded at a scan rate of 50 mV per second. The onset oxidation potentials were estimated from the cyclic voltamograms with the error of ±0.005 eV. The HOMO energy levels were calculated by an empirical formula, HOMO = $-(4.44+E_{onset})$ (eV). The HOMO-LUMO energy gaps (E_g) were obtained from the UV-Vis absorption band edges. The HOMO levels were calculated from the on-set oxidation potentials. The LUMO levels were calculated by summation of the HOMO levels and E_g.

2.5 Quantum chemical calculations and charge transfer analysis

The calculation of the ground state and first singlet electronic excited state of compounds **A**-**G** were performed, using DFT and TDDFT methods [9-10], respectively. Becke's three–parameter hybrid exchange function [11-12], Lee–Yang–Parr gradient-corrected correlation (B3LYP function) [13] and 6-31G(d) basis set [14] were used in both the DFT and TDDFT methods. As TDDFT method was used to study 1,8-naphthalimide [6], benzene [15], and formaldehyde [15] of which excited-state geometries and fluorescence energies were found to be too little affected by the basis set size, TD/B3LYP/6-31G(d) was therefore employed in this work. The structures of all relevant compounds were optimized in dichloromethane solution (dielectric constant = 8.93, at 25 ºC), the solvent effect using the conductor-like polarizable continuum model (CPCM) [16-17] with UAKS cavity model [18]. All calculations were performed with the GAUSSIAN 03 program [19].

3. Results and Discussion

*3.1 Synthesis of **A-F***

The synthesis of target naphthalimide **A-F** started by a condensation reaction between the commercially available 4-bromo-1,8-naphthalic anhydride (**1**) and 2,6-diisopropylaniline in glacial acetic acid to afford naphthalimide **2** in 81% yield (Scheme 1). Nucleophilic substitution of the bromo group by the electron-rich phenol derivatives gave rise to 4-aryloxy-1,8-naphthalimides in excellent yields (**A-E**), whereas the reaction of **2** with the electron-poor methyl 4-hydroxybenzoate afford only low yield of **F** along with unreacted **2**. The yield of **F** was not further optimized as the reaction provided sufficient amount of material for further investigations.

Scheme 1.

3.2 Absorption and emission properties

The photophysical properties of all compounds were investigated in terms of maximum absorption wavelengths (λ_{max}^{ab}), molar absorption coefficients (ε), maximum emission wavelengths (λ_{max}^{em}), and fluorescent quantum yield (Φ). As tabulated in Table 1, the absorption properties of all compounds are relatively similar which imply that the substituent at the 4-position do not significantly influence the electronic states, the energy levels of the ground state and Frank-Condon excited state, of the compounds (Absorption spectra are provided in the supporting information). For the emission, the similar λ_{max}^{em} within the range of 423 to 435 and small stroke shift also indicated a similar radiative decay from their locally excited states.

Table 1 The photophysical and electronic properties of naphthalimide **A-F.**

Compound	Absorption properties		Emission properties		Electronic properties		
	λ_{max}^{abs} (nm)[a]	log ε (M^{-1} cm^{-1})[a]	λ_{max}^{emis} (nm)[b]	Φ[c]	E_g (eV)[d]	HOMO (eV)[e]	LUMO (eV)[f]
A	364	4.32	435	0.002	2.9952	-5.8955	-2.9003
B	364	4.27	434	0.110	3.0244	-6.1036	-3.0792
C	365	4.11	435	0.110	3.0244	-6.1486	-3.1242
D	364	4.18	425	0.840	3.0693	-6.1680	-3.0987
E	360	4.20	423	0.640	3.0617	-6.1036	-3.0419
F	359	4.30	421	0.550	3.0923	-6.2236	-3.1313

[a] Measured in diluted CH_2Cl_2 solution. [b] Excited at 364 nm. [c] Determined by using quinine sulfate in 0.1 M H_2SO_4 as standard reference. [d] Estimated from the electronic absorption onset ($E_g = 1240/\lambda_{onset}$ eV). [e] Calculated from the onset oxidation potential on cyclic voltamograms. [f] Calculated from LUMO = E_g + HOMO.

Despite similarity in the electronic states and radiative decay process, the quantum efficiencies of this set of compounds are drastically different, for instance, the quantum yield of **A** is 0.002 while that of **D** is 0.84. We thus believe that the substituent at the 4-position is responsible for these observed results by means of a photo-induced electron transfer (PET) process. In case of **D**, the HOMO-LUMO level of fluorophore may lie between the large HOMO-LUMO gap of the unactivated phenoxy group (π-π*) (**Figure 1a**). Therefore the PET process could not occur to the excited fluorophore (Flu*). For the electron-rich aryloxyl substituents such as p-methoxyphenoxyl in **A**, p-*tert*-butylphenoxyl in **B** and cumylphenoxyl in

C, their HOMO level might lie in between the HOMO and LUMO level of the fluorophore (**Figure 1b**). Upon the excitation of the fluorophore, the electron from the HOMO of the substituent could transfer to the HOMO of the fluorophore. Subsequent transfer of electron from the fluorophore LUMO to the substituent HOMO could occur and result in low quantum yield.

Figure 1

In contrast, the HOMO level of electron-poor aryloxy group such as p-chlorophenoxyl in **E**, p-carbomethoxyphenoxyl in **F** might be lower than the HOMO level of the fluorophore, but the LUMO level of the aryloxy group might lie between HOMO-LUMO gap (**Figure 1c**). The excited fluorophore can transfer electron to the LUMO of the aryloxy group, then back to the HOMO of the fluorophore.

To investigate the behavior of the relaxation process of the excited states of these compounds, we measured the fluorescence decay times in CH_2Cl_2 solution. The lifetimes of all compounds fitted the biexponential function ($I/I_0 = \alpha_1 \exp[t/\tau_1] + \alpha_2 \exp[t/\tau_2]$) that allowed the calculation of the lifetime components (τ_1 and τ_2) and their average (τ_{ave}) ($\tau_{ave} = a_1\tau_1 + a_2\tau_2$). The radiative rate, k_r, and the non-radiative rate, k_{nr}, can be calculated using equation 1 and 2 [20].

$$k_r = \Phi/\tau_{ave} \qquad (1)$$

$$k_{nr} = (1-\Phi)/\tau_{ave} \qquad (2)$$

The summarized data in Table 2 showed that compounds with electron-rich pendant, i.e. **A**, **B**, and **C**, have high k_{nr}, while compounds with electron-poor pendant, i.e. **E** and **F**, have moderate k_{nr}. As expected, compound **D** has lowest k_{nr} and highest k_r. However, it should be noted that k_{nr} represents the sum of several processes, for example, photo-induced electron transfer, and internal charge-transfer. For compound **A**, the low quantum yield is more likely due to the lower k_r, probably via a greater degree of ICT process which is also supported by the largest Stoke shift observed (Table 1).

Table 2. Fluorescence lifetimes (Biexponential) of naphthalimide **A-F** in CH_2Cl_2 solution.

Compound	Φ^a	a_1	τ_1 (ns)	a_2	τ_2 (ns)	τ_{ave} (ns)	k_r (ns^{-1})	k_{nr} (ns^{-1})
A	0.002	0.11	1.65	0.89	5.30	4.90	0.0004	0.2037
B	0.110	0.94	0.99	0.06	3.10	1.12	0.0982	0.7946
C	0.110	0.98	1.15	0.02	4.53	1.20	0.0917	0.7417
D	0.840	0.46	2.88	0.54	6.21	4.67	0.1799	0.0343
E	0.640	0.05	1.89	0.95	4.05	3.95	0.1620	0.0911
F	0.550	0.67	1.82	0.33	6.51	3.37	0.1632	0.1335

[a] Data taken from **Table 1**.

3.3 Molecular orbital calculations

The optimization of structures of compounds **A-F** in dichloromethane solution obtained by the CPCM(UAKS)–TDDFT/B3LYP/6–31G(d) computations and Mulliken partial charges for their R' groups are shown in Figure 2. As compound **D** emits with highest quantum yield, it was used as the reference compound for determination of charge transfer for other compounds. In order to prove the reliability of our calculation method, an additional compound (**G**) [21] was synthesized and its quantum yield was experimentally measured. This value will later be compared with the calculated value.

Figure 2

The quantum yield for compounds **A**-**F**, Mulliken partial charges for their R' groups and charge transfer to their R' groups are listed in Table 3. It was found that the quantum yields for compounds **A**-**F** vary with their charge transfers and plot of their relationship is shown in Figure 3. It shows fitted lines of four (**A**, **D**, **E** and **F**) and six (all) points of which the fitted equations are Φ = 0.91(±0.08)+2.01(±0.33)Δq and Φ = 0.71(±0.21)+1.74(±0.92)Δq, respectively. The above fitted line shows the high reliability of which the correlation coefficient approachs unity, (r^2=0.9211); the second fitted line has very low reliability of which the correlation coefficient is very low, r^2=0.3390. Nevertheless, x intercept (x value at y = 0 or Δq at Φ=0) for the first and second equations are –0.45(±0.11) and –0.41(±0.34) e, respectively. As the first equation is reliable enough for prediction, it could be used to estimate quantum yield of test compound **G**. It can be point that charge transfer to R' group of compound which is less than –0.455 e, its quantum yield approachs to zero; the cutoff value of charge transfer for equation Φ = 0.91(±0.08)+2.01(±0.33)Δq) is Δq = –0.455 e.

Due to prediction for quantum yield of compound **G** (compound **E** substituted its Cl atom by nitro group), Mulliken partial charges of all atoms of compound **G** obtimized at B3LYP/6–31G(d) level were obtained using CPCM(UAKS)–TDDFT/B3LYP/6–31G(d) method. The B3LYP/6–31G(d)-optimized structure of compound **G** is shown in Figure 4 and its computed partial charges (q = –0.444 e) and charge transfer (Δq = –0.593 e, see Table 2) to NO_2 group were obtained. Due to partial charges and charge transfer for the compound **G**, Δq = –0.593 e, its predicted quantum yield is therefore zero. If (Δq = –0.593 e) charge transfer value for the compound **G** was directedly substitued in equation Φ = 0.91(±0.08)+2.01(±0.33) Δq, its quantum yield (Φ) is –0.28 which is zero. The predicted quantum yield for the compound **G** of zero was found as shown in Figure 3.

Table 3 The experimental quantum yields, computed partial charges, charge transfers and calculated quantum yields of naphthalimide **A-G.**

Compound	*Exp.* Φ^{a}	$q^{\,b,c,d}$	$\Delta q^{\,d,e}$	*Cal.* Φ^{f}
A	0.002	-0.274	-0.423	0.06
B	0.110	-0.006	-0.155	0.60
C	0.110	-0.026	-0.175	0.56
D	0.840	0.149	0.000	0.91
E	0.640	-0.023	-0.172	0.56
F	0.550	-0.070	-0.219	0.47
G	0.002^{g}	-0.444	-0.593	0.00^{h}

[a] Taken from Table 1. [b] Partial charge of their substituents, R', in e. [c] Mulliken charges obtained from the CPCM(UAKS)–TDDFT/B3LYP/6–31G(d) computations, in e. [d] In e. [e] Charge transfer defined as difference between partial charge of their substituents and partial charge of the compound **D**, in e. [f] Computed using equation $\Phi = 0.91(\pm0.08)+2.01(\pm0.33)\Delta q$. [g] see ref. [20], [h] Its charge transfer is less than a cutoff value ($\Delta q = -0.455$ e).

Figure 3

Figure 4

4. Conclusion

Seven derivatives of *N*-(2,6-diisopropylphenyl)-1,8-naphthalimides with an aryloxy substituent at the 4-position were synthesized from the commercially available 4-bromo-1,8-naphthalic anhydride and subjected to a comparative evaluation of the photophysical properties. The results revealed that their quantum efficiencies were exclusively depended on nature of substituents on the aryloxy groups. The compound with a phenoxy group (**D**) exhibited the highest quantum yield, while those compounds with electron-rich or electron-poor aryloxy groups possessed lower quantum efficiencies. It was proposed that quantum yields of these compounds depend the magnitude of electron transfer from fluorophores (1,8-naphthalimide) to their substituents. By CPCM(UAKS)–TDDFT/B3LYP/6–31G(d) computations, the quantum yield (Φ) of these compounds can be theoretically predicted from their charge transfers (Δq) using linear regression equation, $\Phi = 0.91(\pm 0.08)+2.01(\pm 0.33)\ \Delta q$, of which negative quantum yield means zero value. The prediction was later proven as the experimentally determined quantum yield of 4-(4’nitrophenoxyl)-*N*-(2,6-diisopropylphenyl)-1,8-naphthalimides agreed well with the calculated value.

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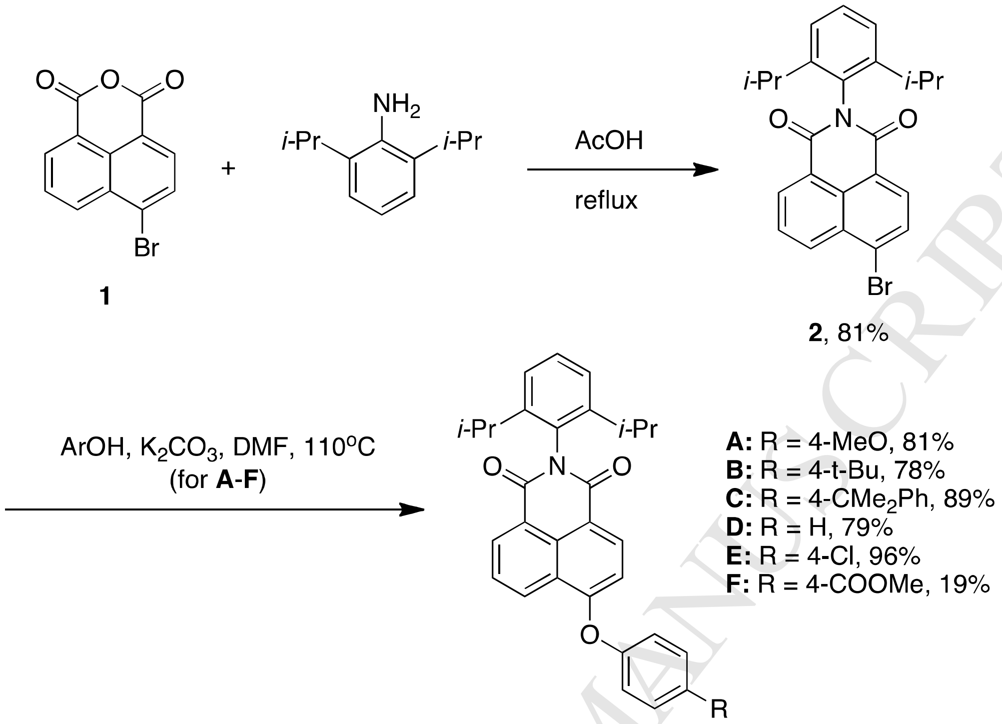
[21] This compound was synthesized from **2** and 4-nitrophenol in 8% yield. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.10 (d, 12H), 2.68 (m, 2H), 7.10 (d, J = 8.0 Hz, 1H), 7.27 (d, J = 7.6 Hz, 2H), 7.40 (t, J = 8.0 Hz, 1H), 8.20-8.30 (m, 4H), 8.52 (d, J = 8.0 Hz, 1H), 8.56 (d, J = 8.0 Hz, 1H), 8.68 (d, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ (ppm): 24.0, 29.2, 114.4, 119.1, 119.3, 123.0, 124.0 124.8, 126.2, 126.4, 127.4, 128.3, 129.6, 130.5, 130.7, 132.7, 132.8, 145.7, 157.1, 161.3, 163.4, 164.0. The quantum yield of 0.002 was determined by using quinine sulfate in 0.1 M H_2SO_4 as standard reference.



Scheme 1 Synthesis of naphthalimide **A-F**

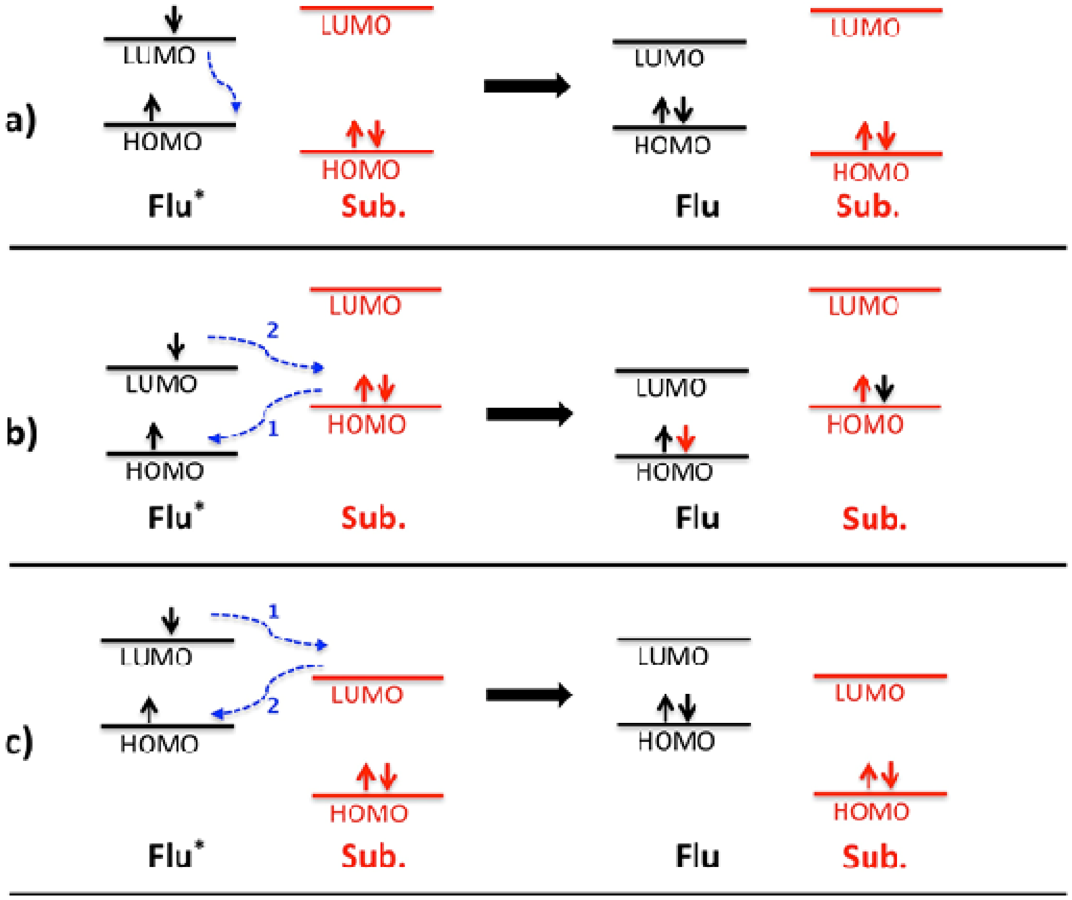


Figure 1. Proposed mechanisms for contribution of substituents' energy levels on PET

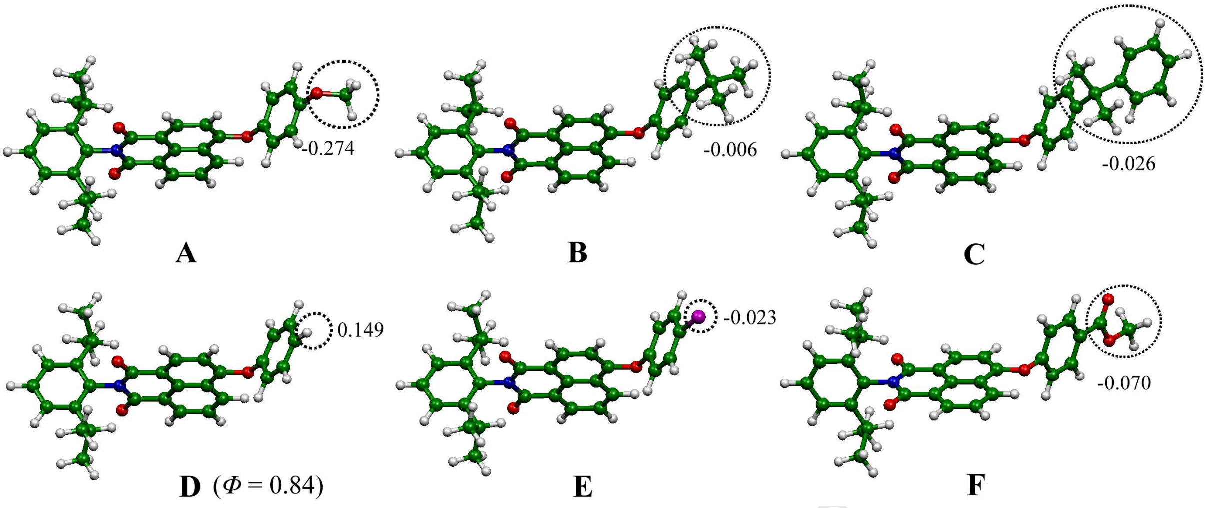


Figure 2. The optimization of structures of compounds **A**-**F**, computed at the CPCM(UAKS)–TDDFT/B3LYP/6–31G(d) level of theory. Compound **D,** R'=H whose partial charge is 0.149 e and which emitts with highest quantum yield, is used as reference compound for charge transfer determination. Mulliken partial charges, in e, for their R' groups are surrounded by dotted lines.

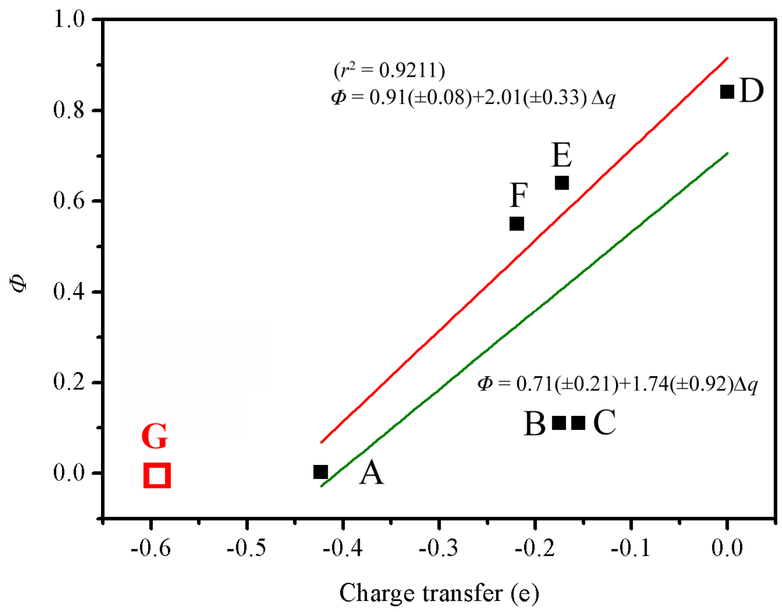
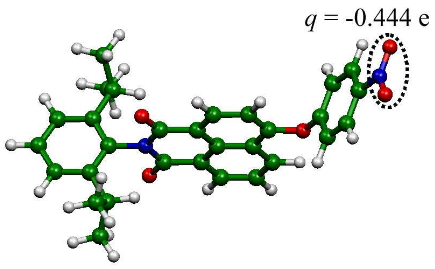


Figure 3. Plot of relationship between quantum yeilds and charge transfers for compounds **A-F**. Above (red line) and bottom (green line) lines are fitted from four (**A**, **D**, **E** and **F**) and six (**A-F**) points data, respectively. The above line (Φ = 0.91(±0.08)+2.01(±0.33)Δq), its cutoff value for charge transfer is Δq = –0.455 e. The red outline square bullet is the predicted plot for tested compound (**G**).



G

Figure 4. The CPCM(UAKS)–TDDFT/B3LYP/6–31G(d)–optimized structure of compound **G** and Mulliken partial charge (*q*= –0.444 e) of its NO_2 group.

Research Highlights

- The substituent effect on quantum yields of 4-aryloxy-N-(2’,6’-diisopropylphenyl)-1,8-naphthalimides was studied.
- The photo-induced electron transfer process was hypothesized and justified by a computational calculation.
- The experimentally determined quantum yield of an additional compound agreed with the calculated value.