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Azo dyes of hexafluoroisopropylidene derivatives: Synthesis and nonlinear optical properties

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Abstract

Two series of fluorine-containing azo dyes containing hexafluoroisopropylidenebis-(4-hydroxybenzene) (B) or 4,4′-(hexafluoroisopropylidene)diphthalicimidine (C) as a backbone connecting the two D-π-A units were synthesized so as to investigate the effects of both the D-π-A units and backbones on the nonlinear optical (NLO) properties of the colourants. Hyper-Rayleigh scattering (HRS) at 1064 nm indicated that the β values of C-containing derivatives were higher than those of B-containing derivatives when the substituents were strongly electron-withdrawing groups. The first hyperpolarizability (β) and static first hyperpolarizability (β_0) of the fluorine-containing dyes increased markedly when the difference between the Hammett constants (σ) [Hammett LP. J Am Chem Soc 1937;59:96. Hansch C, Leo A, Taft RW. Chem Rev 1991;91:165.] of the electron-withdrawing and electron-donating groups in the D-π-A units increased, especially when the electron-withdrawing groups in the D-π-A units were strong, such as in the case of nitro and cyan groups. In addition, UV–vis absorption maximum (λ_{max}) of these fluorine-containing azoic dyes were not red shifted compared with the corresponding mono-D-π-A unit compounds.

Keywords: Fluorine-containing dyes; Nonlinear optical; Backbone; Chromophore; Synthesis; Hammett constants

1. Introduction

Organic nonlinear optical (NLO) materials enjoy usage in optoelectronics and photonics. For them to be practically useful as NLO materials, they must possess high first hyperpolarizability (β) and good optical transparency at the working wavelength [1–3]. Over the past 20 years, extensive efforts have been made in the design and synthesis of many different types of NLO chromophores [4–11], which could be incorporated into macroscopic assemblies to form materials exhibiting large nonlinear optical response [12,13]. In this context, dyes constitute the widest class of organic chromophores investigated and it is known that azo dyes are very effective NLO chromophores [14–16]. In preparing NLO materials, azoic dyes are usually either mixed with polymers or, as D-π-A units, they are inserted in the main polymer chain [17–23]. A survey of data on NLO materials [24–33] revealed that the NLO properties of polymers with the D-π-A units inserted in their main chain could be affected by the backbone that connects the D-π-A unit to the polymer chain. In order to study the effects of both D-π-A units and backbones on NLO properties, this paper concerns the synthesis of two series of fluorine-containing azoic dyes, in which 4,4′-(hexafluoroisopropylidene)diphthalicimidine (C) and hexafluoroisopropylidenebis-(4-hydroxybenzene) (B) were employed, respectively, as molecular backbone, on which two D-π-A units were assembled.

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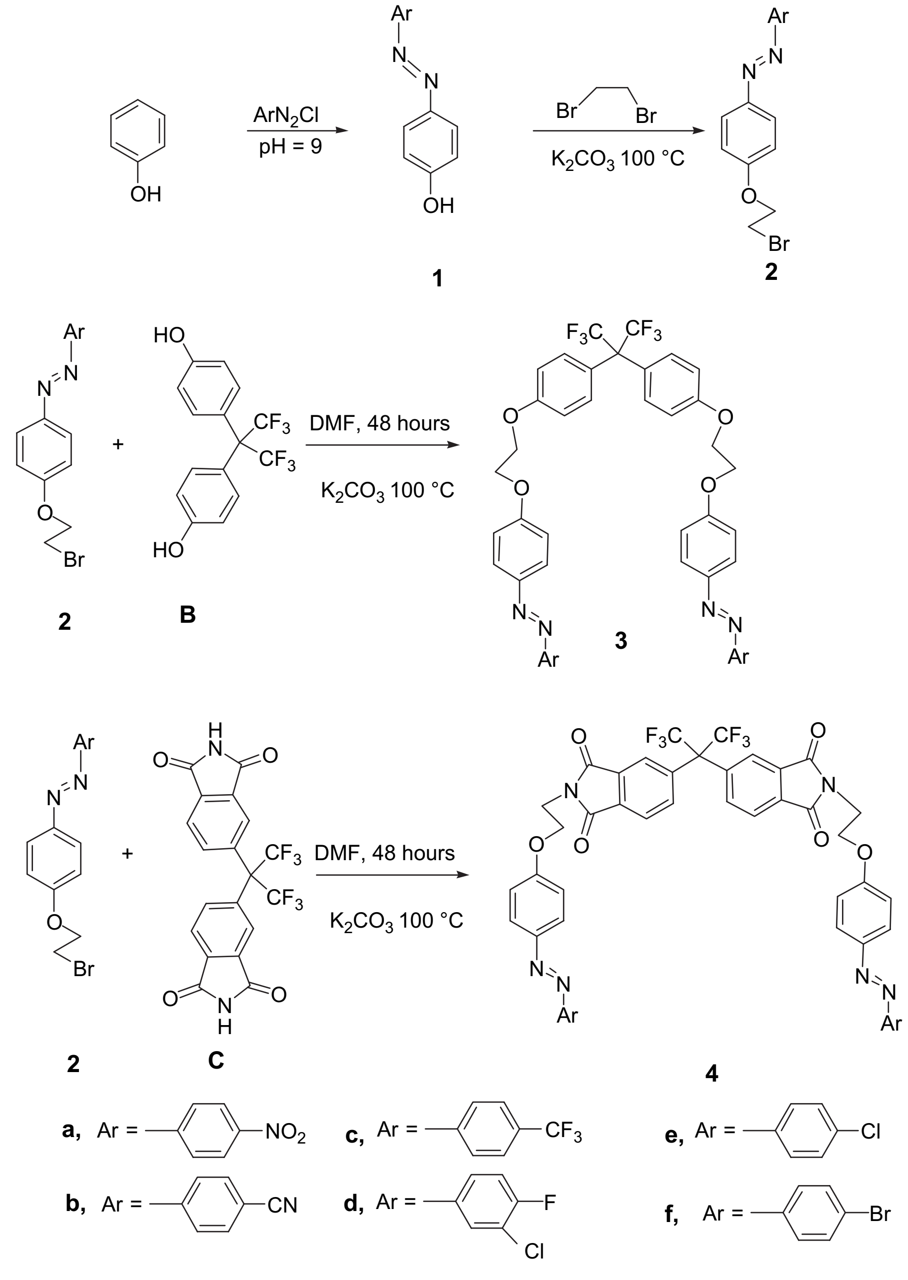
2. Results and discussion

2.1. Synthesis of hexafluoroisopropylidenebis-(4-hydroxybenzene) (B) derivatives and 4,4′-(hexafluoroisopropylidene) diphthalicimidine (C) derivatives

4,4′-(Hexafluoroisopropylidene)diphthalicimidine (C) was synthesized by heating a mixture of 4,4′-(hexafluoroisopropylidene)diphthalic-anhydride and urea [36]. Compounds **2a**, **2b**, **2c**, **2d**, **2e**, and **2f** were synthesized by a two-step procedure (yield: 90–97%). The mono-D-π-A unit compounds (**1a**, **1b**, **1c**, **1d**, **1e**, and **1f**) were prepared by the diazo-coupling reaction of phenol and diazonium salt [37,38] and were then etherified [39] with 1,2-dibromoethane. The fluorine-containing azoic dyes (**3a**, **3b**, **3c**, **3d**, **3e**, and **3f**) were synthesized from etherification of B by compounds **2a**–**2f** (yield: 85–92%) (Scheme 1). Similarly, the fluorine-containing, C-containing derivatives (**4a**, **4b**, **4c**, **4d**, **4e**, and **4f**) were synthesized by nucleophilic substitution of compounds **2a**–**2f** [40] with C in an alkaline solution (yield: 82–87%). Their spectral (^{1}H NMR, IR, Ms) and EA data were in accord with the assigned structures. All of the fluorine-containing azo dyes were soluble in DMF, DMSO, THF, acetone, chloroform, etc., but were insoluble in non-polar solvents.

2.2. Determination of the hyperpolarizability value, β

The hyper-Rayleigh scattering experimental setup was similar to that described in the literature [41,42]. An external



Scheme 1. Synthesis of the chromophores containing two D-π-A units.

reference method (EFM) utilized *para*-nitroaniline (*p*NA) as standard [43]. The popular two-level model could be used to estimate the static first hyperpolarizability (β_0) which reflects the intrinsic polarization of the molecules at zero frequency. The two-level model can be expressed by Eq. (1) [41,44]

$$\beta(\omega)=\frac{\lambda^4}{\left[\left(\lambda^2-\lambda_{\mathrm{gn}}^2\right)\left(\lambda^2-4\lambda_{\mathrm{gn}}^2\right)\right]}\beta_0, \qquad (1)$$

where λ_{gn} is the wavelength corresponding to the transition between the ground and the first excited state, which can be estimated as $\lambda_{\max}$ in the UV–vis absorption spectra; β_0 is related to the oscillator strength, transition energy and the difference between the transition dipole moments of the ground and first excited states. The β and β_0 values of the samples are shown in Table 1.

Hyper-Rayleigh scattering testing at 1064 nm revealed that the β values of the C-containing derivatives were higher than those of the corresponding B-containing derivatives when strongly electron-withdrawing groups were present. Thus, C is a better backbone to connect the D-π-A units to achieve high β in the case of strong electron-withdrawing groups because both the B- and C-containing derivatives can be regarded as two monomeric units connected by a hexafluoroisopropylidene linkage. According to the reports of Yokoyama and co-workers [45–47], the fluorine-containing dyes would have cone-shaped conformation in which two monomeric units were organized noncentrosymmetrically. The monomeric units of both B- and C-containing derivatives have roughly linear conformation with the two monomeric units arranged side by side, giving a relatively stable structure, despite repulsive dipole–dipole interactions [48]. In addition, we can regard the monomeric unit of the C-containing derivatives as having two different D-π-A units linked head-to-tail, whilst the monomeric unit of the B-containing derivatives will have two different D-π-A units linked head-to-head, because a hydroxyethyl group is a stronger electron donor than hexafluoroisopropylidene and the acyl group is a stronger electron acceptor than hexafluoroisopropylidene [34,35]. The monomeric units of the C-containing derivatives would have higher hyperpolarizability, β, due to the cooperative nature of the D-π-A units [48–51]. The results of HRS of the fluorine-containing dyes with two D-π-A units also showed that the first hyperpolarizability increased gradually when the electron-withdrawing ability of the substituents on the benzene ring increased.

Table 1
The $\lambda_{\max}$ of all the compounds in tetrahydrofuran, the first hyperpolarizabilities (β), and static first hyperpolarizabilities (β_0)

Compound	$\lambda_{\max}$ (nm)	Blue shift[a] (nm)	β (10^{-30} esu)[b]	β_0 (10^{-30} esu)
1a	380.8			
2a	360.7			
3a	372.1	8.7	102	46
4a	375.3	5.5	381	168
1b	372.0			
2b	372.0			
3b	360.7	11.3	62	30
4b	364.1	7.9	118	56
1c	357.3			
2c	351.3			
3c	352.9	4.4	47	23
4c	352.9	4.4	53	27
1d	355.2			
2d	350.7			
3d	351.2	4.0	52	26
4d	353.0	2.2	45	23
1e	355.3			
2e	351.1			
3e	351.7	3.6	39	19
4e	355.0	0.3	66	33
1f	357.2			
2f	352.0			
3f	352.8	4.4	49	25
4f	356.0	1.2	39	19

[a] Red shift of $\lambda_{\max}$ was the variation of $\lambda_{\max}$ in THF between chromophores containing two D-π-A units and the corresponding monomer, such as **3a** (**4a**)/**1a**, and **3b** (**4b**)/**1b**.

[b] Data of hyperpolarizabilities (β) of compounds with concentration 10^{-4}–10^{-3} mol L^{-1} were determined at a wavelength of 1064 nm in tetrahydrofuran medium by hyper-Rayleigh scattering (HRS), using *para*-nitroaniline (*p*NA) as the external reference.

As the HRS signals in Fig. 1 show good correlation with solute concentration, any concentration dependent effect, such as aggregation and hydrogen bonding, can be ignored. Local field effects from the solvent can also be ignored, because the D-π-A units of the fluorine-containing dyes are similar and the refractive index change of the solutions of the dyes is negligible. In order to increase the signal-to-noise ratio, a detection bandwidth of 0.3 nm was employed in the HRS experiments.

2.3. Relationship between Hammett constant (σ) [34,35] and hyperpolarizability

The β and β_0 of the fluorine-containing dyes increased when the electron-withdrawing ability of the substituent in the D-π-A units increased from bromo ($\sigma = 0.23$) and chloro ($\sigma = 0.23$) to nitro ($\sigma = 0.78$) (Table 2).

Table 3 shows that the β value of **3a** ($\beta = 102$) was 2.62 times that of **3e** ($\beta = 39$) and the β_0 value of **3a** ($\beta_0 = 46$) was 2.42 times that of **3e** ($\beta_0 = 19$). Similarly, the β of **4a** ($\beta = 381$) was 9.77 times that of **4f** ($\beta = 39$) and the β_0 of **4a** ($\beta_0 = 168$) was 8.84 times that of **4f** ($\beta_0 = 19$). The reason for these findings may be that the dyes containing two D-π-A units with strong electron-withdrawing groups can better delocalise the π electrons in the D-π-A unit [52].

Fig. 2 clearly shows that the β_0 of the fluorine-containing dyes with strong electron-withdrawing groups increased sharply as the $\Delta\sigma$ increased from bromo ($\sigma = 0.23$) and chloro ($\sigma = 0.23$) to nitro ($\sigma = 0.78$) and especially from trifluoromethyl ($\sigma = 0.54$) to nitro ($\sigma = 0.78$). Therefore, only fluorine-containing azo dyes with large $\Delta\sigma$ values should be synthesized if high β_0 is to be achieved.

In addition, Fig. 2 also shows that the β and β_0 of the dyes in which 4,4′-(hexafluoroisopropylidene)diphthalicimidine (C) was employed as backbone were higher than those of the corresponding hexafluoroisopropylidenebis-(4-hydroxybenzene)

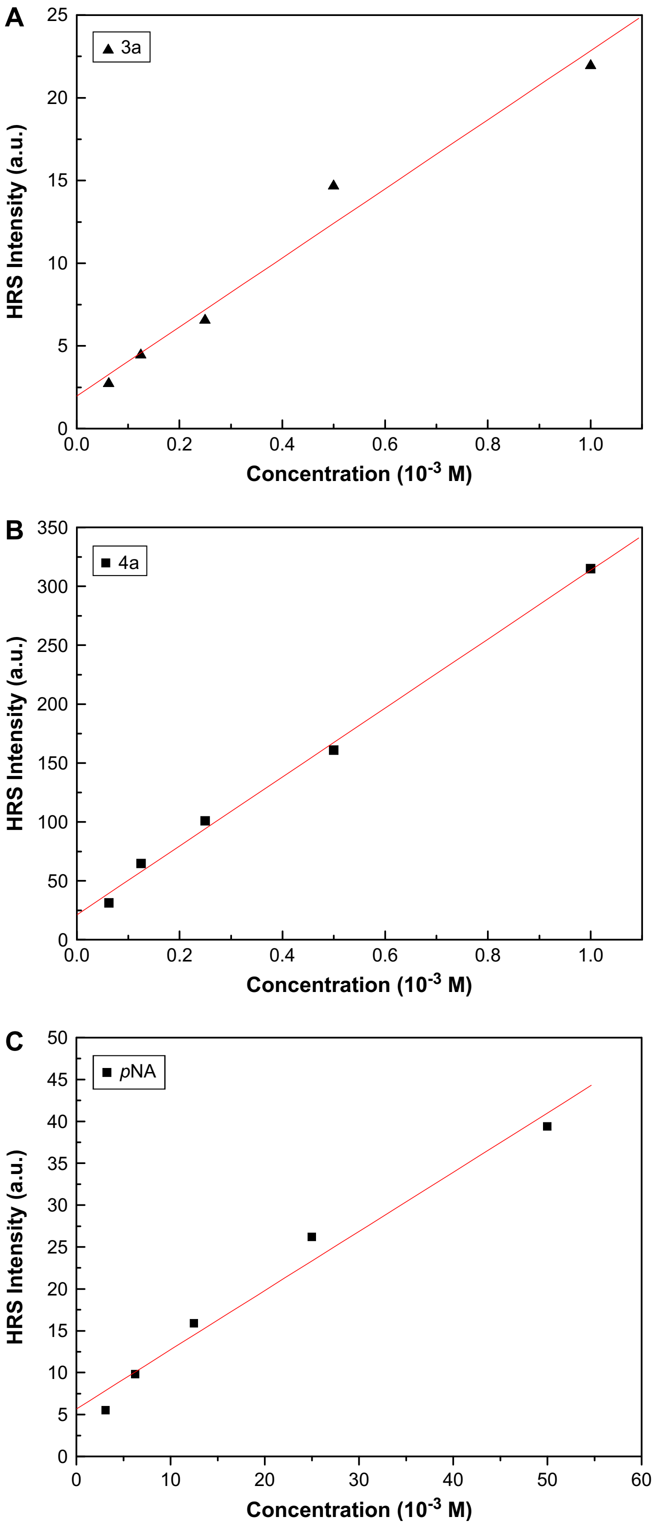


Fig. 1. The first hyperpolarizabilities (β) of the chromophores (**3a**, **4a** and *p*NA). (Part A) HRS intensity versus molar concentration of **3a**. (Part B) HRS intensity versus molar concentration of **4a**. (Part C) HRS intensity versus molar concentration of *p*NA. Solid line is linear fitting of the experimental data.

(B) derivatives when strong electron-withdrawing groups were present. This suggests that C would be a better backbone than B for connecting the D-π-A units to the main chain when there are strong electron-withdrawing groups involved.

2.4. Wavelength of UV–vis absorption maximum

While neither the B- nor the C-containing derivatives produced a red shift of λ_{max}, a slight blue shift (0.3–11.3 nm) (Table 1) was achieved compared to the corresponding mono-D-π-A unit compounds (Fig. 3).

The slight blue shift can be attributed to the fact that the hydroxyl group ($\sigma_P = -0.37$) is a stronger electron donor than the hydroxyethyl group ($\sigma_P = -0.12$) [34,35,53]. In addition, the length of each π-conjugated unit in the dye which contained two D-π-A units was close to that of the corresponding mono-D-π-A unit compound and, also, the number of electrons in each D-π-A unit in the dye that contained two D-π-A units is the same as that in the corresponding mono-D-π-A unit compound.

3. Conclusions

Hyper-Rayleigh scattering revealed that C would be a better backbone to connect the D-π-A units when there are strong electron-withdrawing groups present. The β and β_0 values of the fluorine-containing dyes increased greatly when the difference between the Hammett constants (σ) of the electron-withdrawing and electron-donating groups in the D-π-A units increased, especially when the substituent in the D-π-A units was strongly electron-withdrawing. In addition, the fluorine-containing dyes have good optical transparency at 532 nm. If these fluorine-containing azo dyes were used in fluorine-containing polymers, further systematic investigation of the dyes would give some indication of the most suitable polymer backbone for the introduction of electron-withdrawing and electron-donating groups in D-π-A units.

4. Experimental

Melting points were determined on a Yanaco micro-melting point apparatus (uncorrected). ^{1}H NMR was recorded on a Bruker AM 300 (Germany) and δ was given in ppm (relative to TMS) and coupling constants (J) in Hz. Mass spectra were recorded on a GCMS-QP2010 gas chromatogram mass spectrometer under GC/MS mode. UV–vis spectra were obtain using a Lambda 25 Perkin–Elmer spectrophotometer while IR spectra were recorded on a Brucker Vector 22 spectrophotometer, in which samples were embedded in KBr thin film. Precoated silica gel plates (GF_{254}) were used for analytical TLC. All solvents were purified by standard procedures. All other chemicals were purchased from either Sigma or Aldrich. 4-(4-Nitrophenylazo)phenol [54] (**1a**), 4-(4-hydroxyphenylazo)benzonitrile [55] (**1b**), 4-trifluoromethyl-4′-azobenzenol [56] (**1c**), 4-chloro-4′-azobenzenol [55] (**1e**), and 4-bromo-4′-azobenzenol [57] (**1f**) were synthesized according to the literature.

4.1. Synthesis of 3-chloro-4-fluoro-4′-azobenzenol (*1d*)

A solution of 3-chloro-4-fluoroaniline (0.96 g, 6 mmol) in hydrochloric acid (6 mL, 4 M) was added to sodium nitrite (0.42 g, 6.1 mmol) in 2 mL water and the mixture was stirred

Table 2
Hammett constants σ of electron acceptors and electron donors

Substituent	Nitro	Cyan	Trifluoromethyl	Chloro	Fluoro	Bromo	OCH_2CH_2O–	Hydroxyl
σ_p	0.78	0.66	0.54	0.23	0.06	0.23	−0.12	−0.37
σ_m				0.37				

σ_p and σ_m were, respectively, Hammett constants of *meta*- and *para*-substituted groups in benzene rings.

for 4 h under an N_2 atmosphere at 0–5 °C. Urea (0.01 g, 0.2 mmol) was then added to decompose excess nitrous acid and the mixture was further stirred for 30 min. The solution of the diazonium salt was added to an aqueous solution of phenol (0.62 g, 6.6 mmol), sodium carbonate (3 g), sodium bicarbonate (0.2 g) and ice (15 g) at 0–5 °C; the mixture was stirred for 7 h. After the reaction mixture had been neutralized with a solution of hydrochloric acid (13.6 mL, 3 M), the mixture was filtered. A yellow powder (1.43 g, 5.7 mmol, 95%) was obtained by recrystallization from ethanol and water (18 mL, v/v = 2:1). mp 102–103 °C. ^{1}H NMR ($DCCl_3$): $\delta = 7.97$ (dd, 1H, $^{2}J = 7.0$, $^{3}J = 2.3$, ArH in 3-chloro-4-fluorophenyl), 7.87 (d, 2H, $^{2}J = 8.8$, ArH in phenol), 7.82 (m, 1H, ArH in 3-chloro-4-fluorophenyl), 7.29 (t, 1H, $^{2}J = 8.6$, ArH in 3-chloro-4-fluorophenyl), 6.97 (d, 2H, $^{2}J = 8.8$, ArH in phenol), 5.64 (s, 2H, ArOH). ^{13}C NMR ($DCCl_3$): $\delta = 161.7$, 160.8, 157.5, 150.0, 146.2, 125.6, 124.3, 123.7, 121.7, 117.6, 116.3 (aromatic C). MS (APCI): $m/z = 250.5/252.5$ (abundance ratio: 3/1). Calcd for $C_{12}H_8ClFN_2O$ $[M+H]^+$: 251.0/253.0 (abundance ratio: 3/1). IR (KBr): $\nu = 3260.9$ (br, O–H), 1634.0 (N═N) cm^{-1}. UV–vis (THF): $\lambda_{max} = 355.2$ nm ($\varepsilon = 38{,}240$).

4.2. Synthesis of [4-(2-bromoethoxy)phenyl]-(4-nitrophenyl)diazene (**2a**)

Potassium carbonate (0.5 g) and **1a** (0.55 g, 2 mmol) were added to 1,2-dibromoethane (2 mL, 2.5 g, 13.3 mmol) and the mixture was stirred for 48 h under an N_2 atmosphere at 100 °C. After the reaction mixture was cooled to room temperature, the mixture was filtered and the solvent was evaporated to obtain a yellow solid. The pure product was obtained by recrystallization from acetone (20 mL). Yield: 0.63 g, 1.8 mmol, 90%. mp 155–157 °C. ^{1}H NMR (D_3CCOCD_3): $\delta = 8.39$ (d, 2H, $^{2}J = 8.7$, ArH in 4-nitrophenyl), 8.01 (d, 2H, $^{2}J = 8.7$, ArH in 4-nitrophenyl), 8.00 (d, 2H, $^{2}J = 8.7$, ArH in ethoxybenzene), 7.08 (d, 2H, $^{2}J = 8.7$, ArH in ethoxybenzene), 4.43 (t, 2H, $^{2}J = 6.1$, CH_2), 3.72 (t, 2H, $^{2}J = 6.1$, CH_2). MS: $m/z = 349.0/351.0$ (abundance ratio: 1/1). Calcd for $C_{14}H_{12}BrN_3O_3$ $[M^+]$: 349.0/351.0 (abundance ratio: 1/1). IR (KBr): $\nu = 1600$, 1497 (ArH) cm^{-1}. UV–vis (THF): $\lambda_{max} = 360.7$ nm ($\varepsilon = 35{,}217$).

Table 3
The β_0 of the chromophores and their $\Delta\sigma$

Compound	σ_A[a]	σ_D[a]	$\Delta\sigma$	β_0 (10^{-30} esu)
3a	0.78	−0.12	1.80	46
4a	0.78	−0.12	1.80	168
3b	0.66	−0.12	1.56	30
4b	0.66	−0.12	1.56	56
3c	0.54	−0.12	1.32	23
4c	0.54	−0.12	1.32	27
3d	0.43	−0.12	1.10	26
4d	0.43	−0.12	1.10	23
3e	0.23	−0.12	0.70	19
4e	0.23	−0.12	0.70	33
3f	0.23	−0.12	0.70	25
4f	0.23	−0.12	0.70	19

[a] σ_A and σ_D were, respectively, Hammett constants of electron acceptor and electron donor in benzene rings.

4.3. Synthesis of 4-[4-(2-bromoethoxy)-phenylazo]benzonitrile (**2b**)

Compound **2b** was prepared and purified in a manner similar to **2a**, by using **1b** (0.45 g, 2 mmol) instead of **1a**. A yellow powder (0.63 g, 1.9 mmol, 95%) was obtained by recrystallization from acetone (16 mL). mp 160–162 °C. ^{1}H NMR (D_3CCOCD_3): $\delta = 7.98$ (d, 2H, $^{2}J = 8.1$, ArH in 4-cyanophenyl), 7.81 (d, 2H, $^{2}J = 8.1$, ArH in 4-cyanophenyl), 7.97 (d, 2H, $^{2}J = 8.7$, ArH in ethoxybenzene), 7.07 (d, 2H, $^{2}J = 8.7$, ArH in ethoxybenzene), 4.41 (t, 2H, $^{2}J = 6.0$, CH_2), 3.71 (t, 2H, $^{2}J = 6.0$, CH_2). MS: $m/z = 329.0/331.0$ (abundance ratio: 1/1). Calcd for $C_{15}H_{12}BrN_3O$ $[M^+]$: 329.0/331.0 (abundance ratio: 1/1). IR (KBr): $\nu = 1599$, 1496 (Ar-H) cm^{-1}. UV–vis (THF): $\lambda_{max} = 372.0$ nm ($\varepsilon = 23{,}062$).

4.4. Synthesis of [4-(2-bromoethoxy)phenyl]-(4-trifluoromethylphenyl)diazene (**2c**)

Compound **2c** was prepared and purified in a manner similar to **2a**, by using **1c** (0.53 g, 2 mmol) instead of **1a**. A yellow

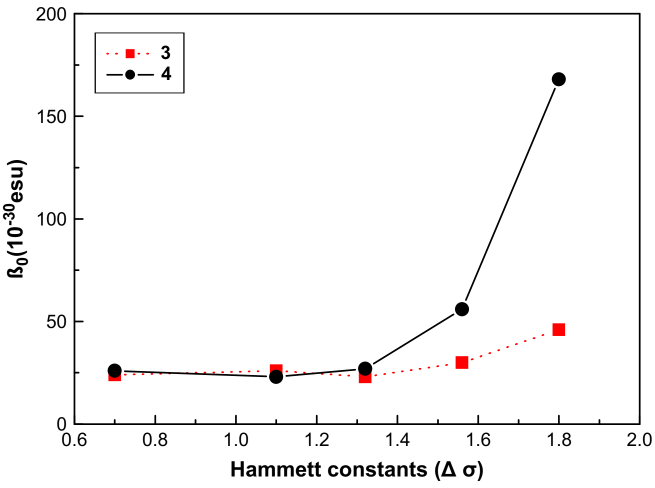


Fig. 2. Relation between the β_0 of these chromophores containing two D-π-A units and their $\Delta\sigma$. Because the σ values of *para*-Cl and *para*-Br are the same, the β_0 is taken as the average of the β_0 of **3e** and that of **3f** (or the average of the β_0 of **4e** and that of **4f**) when $\Delta\sigma$ is equal to 0.7.

powder (0.71 g, 1.9 mmol, 95%) was obtained by recrystallization from acetone (15 mL). mp 98−99 °C. ^{1}H NMR (D_3CCOCD_3): $\delta = 7.98$ (d, 2H, $^2J = 8.3$, ArH in 4-trifluoromethylphenyl), 7.78 (d, 2H, $^2J = 8.3$, ArH in 4-trifluoromethylphenyl), 7.97 (d, 2H, $^2J = 9.0$, ArH in ethoxybenzene), 7.07 (d, 2H, $^2J = 9.0$, ArH in ethoxybenzene), 4.41 (t, 2H, $^2J = 6.0$, CH_2), 3.71 (t, 2H, $^2J = 6.0$, CH_2). MS: $m/z = 372.0/374.0$ (abundance ratio: 1/1). Calcd for $C_{15}H_{12}BrF_3N_2O$ [M^+]: 372.0/374.0 (abundance ratio: 1/1). IR (KBr): $\nu = 1597$, 1499 (Ar-H) cm^{-1}. UV−vis (THF): $\lambda_{max} = 351.3$ nm ($\varepsilon = 25{,}267$).

*4.5. Synthesis of [4-(2-bromoethoxy)phenyl]-(3-chloro-4-fluorophenyl)diazene (**2d**)*

Compound **2d** was prepared and purified in a manner similar to **2a**, by using **1d** (0.50 g, 2 mmol) instead of **1a**. A yellow powder (0.69 g, 1.9 mmol, 97%) was obtained by recrystallization from acetone (15 mL). mp 91−92 °C. ^{1}H NMR (D_3CCOCD_3): $\delta = 7.99$−7.96 (m, 1H, $^2J = 8.3$, ArH in 3-chloro-4-fluorophenyl), 7.84 (m, 1H, $^2J = 8.3$, ArH in ArH in 3-chloro-4-fluorophenyl), 7.30 (m, 1H, $^2J = 8.3$, ArH in ArH in 3-chloro-4-fluorophenyl), 7.93 (d, 2H, $^2J = 8.9$, ArH in ethoxybenzene), 7.05 (d, 2H, $^2J = 8.9$, ArH in ethoxybenzene), 4.40 (t, 2H, $^2J = 6.0$, CH_2), 3.71 (t, 2H, $^2J = 6.0$, CH_2). ^{13}C NMR (D_3CCOCD_3): $\delta = 161.2$, 157.9, 149.7, 147.4, 125.4, 124.3, 124.1, 117.4, 117.1, 115.4 (C in Ar); 68.4, 29.1 (C in CH_2). MS: $m/z = 356.0/358.0/360.0$ (abundance ratio: 3/4/1). Calcd for $C_{14}H_{11}BrClFN_2O$ [M^+]: 356.0/358.0/360.0 (abundance ratio: 3/4/1). IR (KBr): $\nu = 1601$, 1500 (Ar-H) cm^{-1}. UV−vis (THF): $\lambda_{max} = 350.7$ nm ($\varepsilon = 20{,}716$).

*4.6. Synthesis of [4-(2-bromoethoxy)phenyl]-(4-chlorophenyl)diazene (**2e**)*

Compound **2e** was prepared and purified in a manner similar to **2a**, by using **1e** (0.46 g, 2 mmol) instead of **1a**. A yellow powder (0.62 g, 1.8 mmol, 91%) was obtained by recrystallization from acetone (15 mL). mp 138−139 °C. ^{1}H NMR (D_3CCOCD_3): $\delta = 7.94$ (d, 2H, $^2J = 8.8$, ArH in 4-chlorophenyl), 7.86 (d, 2H, $^2J = 9.0$, ArH in ethoxybenzene), 7.50 (d, 2H, $^2J = 8.8$, ArH in 4-chlorophenyl), 7.06 (d, 2H, $^2J = 9.0$, ArH in ethoxybenzene), 4.41 (t, 2H, $^2J = 6.0$, CH_2), 3.71 (t, 2H, $^2J = 6.0$, CH_2). ^{13}C NMR (D_3CCOCD_3): $\delta = 161.1$, 151.4, 147.6, 136.7, 129.7, 125.3, 124.3, 115.3 (C in Ar); 68.4, 29.1 (in CH_2). MS: $m/z = 338.0/340.0/342.0$ (abundance ratio: 3/4/1). Calcd for $C_{14}H_{12}BrClN_2O$ [M^+]: 338.0/340.0/342.0 (abundance ratio: 3/4/1). IR (KBr): $\nu = 1600$, 1498 (Ar-H) cm^{-1}. UV−vis (THF): $\lambda_{max} = 351.1$ nm ($\varepsilon = 23{,}469$).

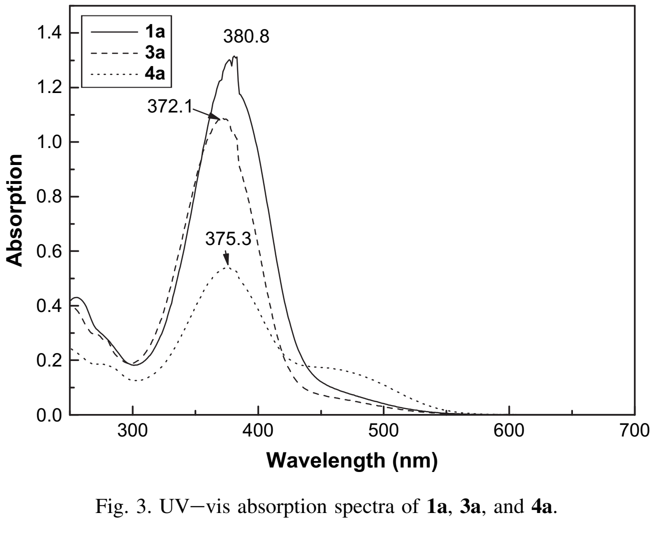


Fig. 3. UV−vis absorption spectra of **1a**, **3a**, and **4a**.

*4.7. Synthesis of [4-(2-bromoethoxy)phenyl]-(4-bromophenyl)diazene (**2f**)*

Compound **2f** was prepared and purified in a manner similar to **2a**, by using **1f** (0.51 g, 2 mmol) instead of **1a**. A yellow powder (0.73 g, 1.9 mmol, 94%) was obtained by recrystallization from acetone (17 mL). mp 135−137 °C. ^{1}H NMR (D_3CCOCD_3): $\delta = 7.94$ (d, 2H, $^2J = 9.0$, ArH in 4-bromophenyl), 7.78 (d, 2H, $^2J = 8.7$, ArH in ethoxybenzene), 7.65 (d, 2H, $^2J = 9.0$, ArH in 4-bromophenyl), 7.05 (d, 2H, $^2J = 8.7$, ArH in ethoxybenzene), 4.42 (t, 2H, $^2J = 6.3$, CH_2), 3.70 (t, 2H, $^2J = 6.3$, CH_2). MS (GC/MS): $m/z = 382.0/384.0/386.0$ (abundance ratio: 1/2/1). Calcd for $C_{14}H_{12}Br_2N_2O$ [M^+]: 381.9/383.9/385.9 (abundance ratio: 1/2/1). IR (KBr): $\nu = 1600$, 1497 (Ar-H) cm^{-1}. UV−vis (THF): $\lambda_{max} = 352.0$ nm ($\varepsilon = 22{,}476$).

*4.8. Synthesis of 2,2-bis[4-[2-[4-[(4-nitrophenyl)azo]-phenoxy]ethoxy]phenyl]hexafluoropropane (**3a**)*

Potassium carbonate (0.2 g), hexafluoroisopropylidenebis-(4-hydroxybenzene) (B) (45 mg, 0.15 mmol) and **2a** (105 mg, 0.3 mmol) were added to *N*,*N*-dimethylformamide (5 mL) and the mixture was stirred for 48 h under an N_2 atmosphere at 100 °C. After the reaction mixture was cooled to room temperature, it was filtered and the solvent was evaporated to obtain a yellow solid. The pure product was obtained by recrystallization from methanol and water (20 mL, v/v = 1:1). Yield: 112 mg, 0.13 mmol, 86%. mp 140−142 °C. ^{1}H NMR (D_3CCOCD_3): $\delta = 8.45$ (d, 4H, $^2J = 8.8$, ArH in 4-nitrophenyl), 8.13 (d, 4H, $^2J = 8.8$, ArH in 4-nitrophenyl), 8.05 (d, 4H, $^2J = 8.9$, ArH in ethoxybenzene), 7.26 (d, 4H, $^2J = 8.9$, ArH in ethoxybenzene), 8.37 (d, 4H, $^2J = 8.7$, ArH in cymene), 7.13 (d, 4H, $^2J = 8.7$, ArH in cymene), 4.62 (t, 4H, $^2J = 6.0$, CH_2), 4.54 (t, 4H, $^2J = 6.0$, CH_2). Anal. Calcd for $C_{43}H_{32}F_6N_6O_8$ (874.2): C, 59.00; H, 3.73; N, 9.65. Found: C, 59.04; H, 3.69; N, 9.61. IR (KBr): $\nu = 1599.4$, 1500.1 (Ar-H) cm^{-1}. UV−vis (THF): $\lambda_{max} = 372.1$ nm ($\varepsilon = 44{,}751$).

*4.9. Synthesis of 2,2-bis[4-[2-[4-[(4-cyanophenyl)-azo]phenoxy]ethoxy]phenyl]hexafluoropropane (**3b**)*

Compound **3b** was prepared and purified in a manner similar to **3a**, by using **2b** (99 mg, 0.3 mmol) instead of **2a**. A yellow powder (110 mg, 0.13 mmol, 88%) was obtained by recrystallization from methanol and water (20 mL, v/v = 1:1). mp 175–178 °C. ^{1}H NMR (D_3CCOCD_3): $\delta = 8.13$ (d, 4H, $^2J = 8.1$, ArH in 4-cyanophenyl), 8.05 (d, 4H, $^2J = 8.1$, ArH in 4-cyanophenyl), 7.97 (d, 4H, $^2J = 8.9$, ArH in ethoxybenzene), 7.25 (d, 4H, $^2J = 8.9$, ArH in ethoxybenzene), 7.37 (d, 4H, $^2J = 8.7$, ArH in cymene), 7.13 (d, 4H, $^2J = 8.7$, ArH in cymene), 4.57 (s, 4H, CH_2), 4.53 (s, 4H, CH_2). Anal. Calcd for $C_{45}H_{32}F_6N_6O_4$ (834.8): C, 64.75; H, 3.86; N, 10.07. Found: C, 64.67; H, 3.90; N, 10.13. IR (KBr): $\nu = 1664$ (N=N), 1600, 1500 (Ar-H) cm^{-1}. UV–vis (THF): $\lambda_{max} = 360.7$ nm ($\varepsilon = 43{,}588$).

*4.10. Synthesis of 2,2-bis[4-[2-[4-[(4-trifluoromethylphenyl)azo]phenoxy]-ethoxy]phenyl]-hexafluoropropane (**3c**)*

Compound **3c** was prepared and purified in a manner similar to **3a**, by using **2c** (112 mg, 0.3 mmol) instead of **2a**. A yellow powder (121 mg, 0.13 mmol, 88%) was obtained by recrystallization from methanol and water (18 mL, v/v = 1:1). mp 102–105 °C. ^{1}H NMR (D_3CCOCD_3): $\delta = 8.01$ (d, 4H, $^2J = 8.1$, ArH in 4-trifluoromethylphenyl), 7.52 (d, 4H, $^2J = 8.1$, ArH in 4-trifluoromethylphenyl), 7.99 (d, 4H, $^2J = 8.9$, ArH in ethoxybenzene), 7.22 (d, 4H, $^2J = 8.9$, ArH in ethoxybenzene), 7.37 (d, 4H, $^2J = 8.7$, ArH in cymene), 7.12 (d, 4H, $^2J = 8.7$, ArH in cymene), 4.55 (s, 4H, CH_2), 4.52 (s, 4H, CH_2). Anal. Calcd for $C_{45}H_{32}F_{12}N_4O_4$ (920.7): C, 58.70; H, 3.50; N, 6.08. Found: C, 58.60; H, 3.58; N, 6.12. IR (KBr): $\nu = 1644$ (N=N), 1598, 1499 (Ar-H) cm^{-1}. UV–vis (THF): $\lambda_{max} = 352.9$ nm ($\varepsilon = 37{,}170$).

*4.11. Synthesis of 2,2-bis[4-[2-[4-[(3-chloro-4-fluorophenyl)azo]phenoxy]ethoxy]phenyl]-hexafluoropropane (**3d**)*

Compound **3d** was prepared and purified in a manner similar to **3a**, by using **2d** (107 mg, 0.3 mmol) instead of **2a**. A yellow powder (121 mg, 0.14 mmol, 91%) was obtained by recrystallization from methanol and water (15 mL, v/v = 1:1). mp 158–160 °C. ^{1}H NMR (D_3CCOCD_3): $\delta = 8.09$ (s, 2H, ArH in 3-chloro-4-fluorophenyl), 8.05 (d, 4H, $^2J = 8.9$, ArH in ethoxybenzene), 8.02 (d, 2H, $^2J = 8.9$, ArH in 3-chloro-4-fluorophenyl), 7.93 (d, 2H, $^2J = 8.9$, ArH in 3-chloro-4-fluorophenyl), 7.25 (d, 4H, $^2J = 8.9$, ArH in ethoxybenzene), 7.37 (d, 4H, $^2J = 8.4$, ArH in cymene), 7.13 (d, 4H, $^2J = 8.4$, ArH in cymene), 4.58 (d, 4H, $^2J = 5.0$, CH_2), 4.53 (d, 4H, $^2J = 5.0$, CH_2). Anal. Calcd for $C_{43}H_{30}Cl_2F_8N_4O_4$ (889.6): C, 58.05; H, 3.40; N, 6.30. Found: C, 58.00; H, 3.42; N, 6.35. IR (KBr): $\nu = 1651$ (N=N), 1601, 1501 (Ar-H) cm^{-1}. UV–vis (THF): $\lambda_{max} = 351.2$ nm ($\varepsilon = 36{,}261$).

*4.12. Synthesis of 2,2-bis[4-[2-[4-[(4-chlorophenyl)azo]-phenoxy]ethoxy]phenyl]hexafluoropropane (**3e**)*

Compound **3e** was prepared and purified in a manner similar to **3a**, by using **2e** (102 mg, 0.3 mmol) instead of **2a**. A yellow powder (118 mg, 0.14 mmol, 92%) was obtained by recrystallization from methanol and water (15 mL, v/v = 1:1). mp 208–210 °C. ^{1}H NMR (D_3CCOCD_3): $\delta = 8.00$ (d, 4H, $^2J = 8.9$, ArH in 4-chlorophenyl), 7.61 (d, 4H, $^2J = 8.9$, ArH in 4-chlorophenyl), 7.92 (d, 4H, $^2J = 8.9$, ArH in ethoxybenzene), 7.23 (d, 4H, $^2J = 8.9$, ArH in ethoxybenzene), 7.37 (d, 4H, $^2J = 7.8$, ArH in cymene), 6.93 (d, 4H, $^2J = 7.8$, ArH in cymene), 4.61 (d, 4H, $^2J = 6.0$, CH_2), 4.54 (d, 4H, $^2J = 6.0$, CH_2). Anal. Calcd for $C_{43}H_{32}Cl_2F_6N_4O_4$ (853.6): C, 60.50; H, 3.78; N, 6.56. Found: C, 60.45; H, 3.82; N, 6.60. IR (KBr): $\nu = 1645$ (N=N), 1599, 1501 (Ar-H) cm^{-1}. UV–vis (THF): $\lambda_{max} = 351.7$ nm ($\varepsilon = 27{,}762$).

*4.13. Synthesis of 2,2-bis[4-[2-[4-[(4-bromophenyl)azo]-phenoxy]ethoxy]phenyl]hexafluoropropane (**3f**)*

Compound **3f** was prepared and purified in a manner similar to **3a**, by using **2f** (115 mg, 0.3 mmol) instead of **2a**. A yellow powder (120 mg, 0.13 mmol, 85%) was obtained by recrystallization from methanol and water (20 mL, v/v = 1:1). mp 182–184 °C. ^{1}H NMR (D_3CCOCD_3): $\delta = 7.97$ (d, 4H, $^2J = 8.4$, ArH in 4-bromophenyl), 7.77 (d, 4H, $^2J = 8.4$, ArH in 4-bromophenyl), 7.85 (d, 4H, $^2J = 8.9$, ArH in ethoxybenzene), 7.22 (d, 4H, $^2J = 8.9$, ArH in ethoxybenzene), 7.36 (d, 4H, $^2J = 7.2$, ArH in cymene), 6.92 (d, 4H, $^2J = 7.2$, ArH in cymene), 4.62 (d, 4H, $^2J = 6.6$, CH_2), 4.50 (d, 4H, $^2J = 6.6$, CH_2). Anal. Calcd for $C_{43}H_{32}Br_2F_6N_4O_4$ (942.5): C, 54.79; H, 3.42; N, 5.96. Found: C, 54.73; H, 3.48; N, 6.01. IR (KBr): $\nu = 1647$ (N=N), 1600, 1499 (Ar-H) cm^{-1}. UV–vis (THF): $\lambda_{max} = 352.8$ nm ($\varepsilon = 47{,}485$).

*4.14. Synthesis of 5,5′-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis-[2-(2-[4-[(4-nitrophenyl)azo]phenoxy]ethoxy)-1H-isoindole-1,3(2H)-dione] (**4a**)*

Potassium carbonate (0.2 g), 4,4′-(hexafluoroisopropylidene)diphthalicimidine (C) (66 mg, 0.15 mmol) and **2a** (105 mg, 0.3 mmol) were added to *N*,*N*-dimethylformamide (5 mL), and the mixture was stirred for 48 h under an N_2 atmosphere at 100 °C. After the reaction mixture was cooled to room temperature, it was filtered and the solvent was evaporated to obtain a yellow solid. The pure product was obtained by recrystallization from methanol and water (20 mL, v/v = 1:1). Yield: 120 mg, 0.12 mmol, 82%. mp 148–150 °C. ^{1}H NMR (D_3CCOCD_3): $\delta = 8.43$ (d, 4H, $^2J = 8.8$, ArH in 4-nitrophenyl), 8.10 (d, 4H, $^2J = 8.8$, ArH in 4-nitrophenyl), 8.07 (d, 4H, $^2J = 8.9$, ArH in ethoxybenzene), 7.16 (d, 4H, $^2J = 8.9$, ArH in ethoxybenzene), 7.91 (s, 2H, ArH in cymene), 7.70 (d, 2H, $^2J = 8.7$, ArH in cymene), 6.91 (d, 2H, $^2J = 8.7$, ArH in cymene), 4.42 (t, 4H, $^2J = 6.0$, CH_2), 3.80 (t, 4H, $^2J = 6.0$, CH_2). Anal. Calcd for $C_{47}H_{30}F_6N_8O_{10}$ (980.2): C, 57.56; H, 3.08; N, 11.42. Found: C, 57.49; H, 3.08; N, 11.48. IR (KBr): $\nu = 1720$ (C=O), 1603, 1501 (ArH) cm^{-1}. UV–vis (THF): $\lambda_{max} = 375.3$ nm ($\varepsilon = 34{,}830$).

*4.15. Synthesis of 5,5′-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis-[2-(2-[4-[(4-cyanophenyl)azo]phenoxy]ethoxy)-1H-isoindole-1,3(2H)-dione] (**4b**)*

Compound **4b** was prepared and purified in a manner similar to **4a**, by using **2b** (99 mg, 0.3 mmol) instead of **2a**. A yellow powder (123 mg, 0.13 mmol, 87%) was obtained by recrystallization from methanol and water (20 mL, v/v = 1:1). mp 189–192 °C. ^{1}H NMR (D_3CCOCD_3): $\delta = 8.13{-}7.89$ (m, 12H, ArH), 7.21 (d, 4H, $^2J = 8.9$, ArH in ethoxybenzene), 7.75 (s, 2H, ArH in cymene), 7.60 (d, 2H, $^2J = 8.7$, ArH in cymene), 7.18 (d, 2H, $^2J = 8.7$, ArH in cymene), 4.37 (t, 4H, $^2J = 6.0$, CH_2), 3.86 (t, 4H, $^2J = 6.0$, CH_2). Anal. Calcd for $C_{49}H_{30}F_6N_8O_6$ (940.2): C, 62.56; H, 3.21; N, 11.91. Found: C, 62.49; H, 3.25; N, 11.99. IR (KBr): $\nu = 1720$ (C=O), 1656 (N=N), 1601, 1501 (Ar-H) cm^{-1}. UV–vis (THF): $\lambda_{max} = 364.1$ nm ($\varepsilon = 28{,}666$).

*4.16. Synthesis of 5,5′-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis-[2-(2-[4-[(4-trifluoromethylphenyl)azo]-phenoxy]ethoxy)-1H-isoindole-1,3(2H)-dione] (**4c**)*

Compound **4c** was prepared and purified in a manner similar to **4a**, by using **2c** (112 mg, 0.3 mmol) instead of **2a**. A yellow powder (132 mg, 0.13 mmol, 86%) was obtained by recrystallization from methanol and water (18 mL, v/v = 1:1). mp 154–156 °C. ^{1}H NMR (D_3CCOCD_3): $\delta = 8.13{-}7.89$ (m, 12H, ArH), 7.19 (d, 4H, $^2J = 8.9$, ArH in ethoxybenzene), 7.71 (s, 2H, ArH in cymene), 7.60 (d, 2H, $^2J = 8.7$, ArH in cymene), 7.00 (d, 2H, $^2J = 8.7$, ArH in cymene), 4.60 (t, 4H, $^2J = 6.0$, CH_2), 4.48 (t, 4H, $^2J = 6.0$, CH_2). Anal. Calcd for $C_{49}H_{30}F_{12}N_6O_6$ (1026.2): C, 57.32; H, 2.94; N, 8.18. Found: C, 57.26; H, 2.98; N, 8.23. IR (KBr): $\nu = 1600$, 1500 (Ar-H) cm^{-1}. UV–vis (THF): $\lambda_{max} = 352.9$ nm ($\varepsilon = 60{,}722$).

*4.17. Synthesis of 5,5′-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis-[2-(2-[4-[(3-chloro-4-fluorophenyl)azo]phenoxy]-ethoxy)-1H-isoindole-1,3(2H)-dione] (**4d**)*

Compound **4d** was prepared and purified in a manner similar to **4a**, by using **2d** (107 mg, 0.3 mmol) instead of **2a**. A yellow powder (128 mg, 0.13 mmol, 86%) was obtained by recrystallization from methanol and water (20 mL, v/v = 1:1). mp 125–128 °C. ^{1}H NMR (D_3CCOCD_3): $\delta = 8.13{-}7.90$ (m, 12H, ArH), 7.25 (d, 4H, $^2J = 8.9$, ArH in ethoxybenzene), 7.85 (s, 2H, ArH in cymene), 7.45 (d, 2H, $^2J = 8.7$, ArH in cymene), 6.95 (d, 2H, $^2J = 8.7$, ArH in cymene), 4.51 (m, 8H, 4× CH_2). Anal. Calcd for $C_{47}H_{28}Cl_2F_8N_6O_6$ (995.7): C, 56.70; H, 2.83; N, 8.44. Found: C, 56.63; H, 2.84; N, 8.48. IR (KBr): $\nu = 1721$ (C=O), 1647 (N=N), 1598, 1498 (Ar-H) cm^{-1}. UV–vis (THF): $\lambda_{max} = 353.0$ nm ($\varepsilon = 34{,}531$).

*4.18. Synthesis of 5,5′-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis-[2-(2-[4-[(4-chlorophenyl)azo]phenoxy]ethoxy)-1H-isoindole-1,3(2H)-dione] (**4e**)*

Compound **4e** was prepared and purified in a manner similar to **4a**, by using **2e** (102 mg, 0.3 mmol) instead of **2a**. A yellow powder (122 mg, 0.13 mmol, 85%) was obtained by recrystallization from methanol and water (15 mL, v/v = 1:1). mp 135–138 °C. ^{1}H NMR (D_3CCOCD_3): $\delta = 7.94$ (d, 4H, $^2J = 9.0$, ArH in 4-chlorophenyl), 7.66 (d, 4H, $^2J = 9.0$, ArH in 4-chlorophenyl), 7.91 (d, 4H, $^2J = 8.9$, ArH in ethoxybenzene), 7.16 (d, 4H, $^2J = 8.9$, ArH in ethoxybenzene), 7.81 (s, 2H, ArH in cymene), 7.57 (d, 2H, $^2J = 8.7$, ArH in cymene), 6.81 (d, 2H, $^2J = 8.7$, ArH in cymene), 4.31 (t, 4H, $^2J = 6.0$, CH_2), 3.86 (t, 4H, $^2J = 6.0$, CH_2). Anal. Calcd for $C_{47}H_{30}Cl_2F_6N_6O_6$ (958.2): C, 58.82; H, 3.15; N, 8.76. Found: C, 58.78; H, 3.10; N, 8.82. IR (KBr): $\nu = 1718$ (C=O), 1644 (N=N), 1601, 1500 (Ar-H) cm^{-1}. UV–vis (THF): $\lambda_{max} = 355.4$ nm ($\varepsilon = 31{,}794$).

*4.19. Synthesis of 5,5′-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis-[2-(2-[4-[(4-bromophenyl)azo]phenoxy]ethoxy)-1H-isoindole-1,3(2H)-dione] (**4f**)*

Compound **4f** was prepared and purified in a manner similar to **4a**, by using **2f** (115 mg, 0.3 mmol) instead of **2a**. A yellow powder (135 mg, 0.13 mmol, 86%) was obtained by recrystallization from methanol and water (20 mL, v/v = 1:1). mp 198–200 °C. ^{1}H NMR (D_3CCOCD_3): $\delta = 7.94$ (d, 4H, $^2J = 9.0$, ArH in 4-bromophenyl), 7.83 (d, 4H, $^2J = 9.0$, ArH in 4-bromophenyl), 7.92 (d, 4H, $^2J = 8.9$, ArH in ethoxybenzene), 7.14 (d, 4H, $^2J = 8.9$, ArH in ethoxybenzene), 8.03 (s, 2H, ArH in cymene), 7.75 (d, 2H, $^2J = 8.7$, ArH in cymene), 7.11 (d, 2H, $^2J = 8.7$, ArH in cymene), 4.34 (t, 4H, $^2J = 6.3$, CH_2), 3.85 (t, 4H, $^2J = 6.3$, CH_2). Anal. Calcd for $C_{47}H_{30}Br_2F_6N_6O_6$ (1048.6): C, 53.84; H, 2.88; N, 8.01. Found: C, 53.78; H, 2.93; N, 8.07. IR (KBr): $\nu = 1719$ (C=O), 1651 (N=N), 1601, 1501 (Ar-H) cm^{-1}. UV–vis (THF): $\lambda_{max} = 356.0$ nm ($\varepsilon = 25{,}754$).

4.20. First hyperpolarizability, β

The HRS experimental setup we used is similar to that described in the literature [41,42]. A Q-switched Nd:YAG laser pulse (Continuum Precision II, 10 Hz, 8–10 ns pulse width) at 1064 nm was focused by a lens ($f = 50$ cm) into a cylindrical cell (K9-glass, 50 mm in length, 3 mm in radius). The pump energy could be adjusted by rotating a half-wave plate and was adjusted to <0.1 mJ by an energy meter. An interference filter at 532 nm (0.3 nm bandwidth) was mounted at the entrance of the photomultiplier tube (PMT, GDB159) to prevent luminescence at other wavelengths. The HRS signals were detected and averaged by a high frequency digital oscilloscope (Tektronix TDS 3052, 500 MHz). An external reference method (EFM) was used by choosing *para*-nitroaniline (*p*NA) as standard [43]. The

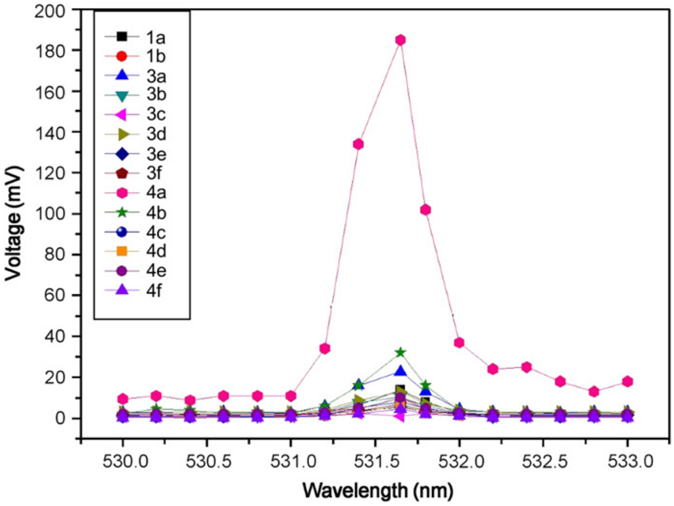


Fig. 4. Hyper-Rayleigh scattering spectra of chromophores.

sample under test and *p*NA were dissolved in THF and concentration gradients of the samples were created by successive dilution. The first hyperpolarizability of *p*NA in THF was known to be 21.4 × 10^{-30} esu [43]. For a two-component solution, the HRS intensity $I_{2\omega}$ could be calculated by Eq. (2) [58],

$$I_{2\omega} = G\left(N_1\langle\beta_1^2\rangle + N_2\langle\beta_2^2\rangle\right)(I_\omega)^2 \mathrm{e}^{-N_2\alpha_2 l}, \tag{2}$$

where I_ω is the incident intensity, G is a parameter reflecting experimental conditions such as instrumental factors, collection efficiency and local field corrections, N is the number density and the subscripts 1 and 2 refer to the solvent and the solute, respectively. The angular brackets indicate the spatial orientational average of the chromophore molecules within the focus area with orientational fluctuations and density fluctuations. The factor $\mathrm{e}^{-N_2\alpha_2 l}$ accounts for the losses of HRS signal due to the linear absorption and scattering of the solution at 532 nm.

The extent of fluorescence around 532 nm (530−533 nm) was measured using a fluorescence spectrometer (Edinburgh, FLS920) [59]. The hyper-Rayleigh scattering spectra are shown in Fig. 4 from which it is evident that the 12 fluorine-containing dyes displayed sharp peak with a bandwidth of 0.3 nm at 531.8 nm with no other signals nearby. Since there was no background signal from 530 to 533 nm, HRS measurements using a 532 nm interference filter with a bandwidth of 0.3 nm should therefore provide the same results as in the spectral measurement above. These findings were considered to show that the β values obtained were valid.

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