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Synthesis and properties of a new second-order NLO chromophore containing the benzo[b]furan moiety for electro-optical materials

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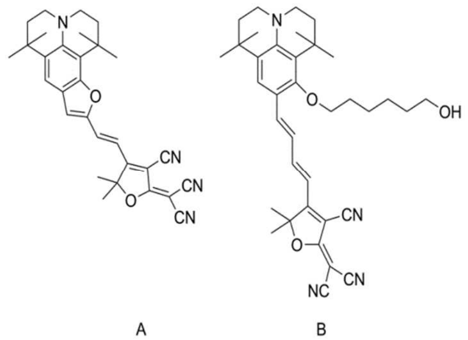
To further explored the potential application of the benzo[b]furan ring in NLO chromophores. We have designed and synthesized a new chromophore (A) having 1,1,7,7-Tetramethyljulolidine fused furan ring as the electron donor group to systematically investigate the role of benzo[b]furan ring in NLO chromophores. Its corresponding chromophore B using 8-(1-hydroxyhexoxy)-1,1,7,7-Tetramethyljulolidine as electron donor group was also prepared for comparison. Upon introducing benzo[b]furan ring at the donor end of chromophore A, a reduced energy gap of 1.14 eV was obtained compared with chromophore B (E_{ge} = 1.28 eV). Furthermore, the macroscopic EO activity of the new chromophores were investigated by guest-host doped polymer films (doping chromophores A or B into amorphous polycarbonate (APC) with a loading density of 20 wt%). The poled films containing chromophore A achieved a maximum EO coefficients (r_{33}) of 52 pm/V at 1310 nm, which is larger than the poled films containing chromophore B (r_{33} = 35 pm/V). These two chromophores showed excellent thermal stability with the onset decomposition temperatures higher than 229 °C. The combined large EO activities and high thermal stability indicates the important role of the benzo[b]furan moiety in the construction of new NLO chromophores.

Introduction

Recently, high-performance organic electro-optic (EO) materials have been drawn great attention for its extensive potential application in telecommunications, optical modulation and optical memory.[1, 2] In principle, large bulk EO response of a material depends on large microscopic molecular hyperpolarizabilities (β) of a dipolar chromophore. Generally, traditional nonlinear optical (NLO) dipolar chromophores are commonly consist of a π-conjugated bridge end-capped with electron donor and acceptor substituents. Structure-property relationships that have been established indicate that large β values of the chromophores can be achieved by careful modification of the strength of donor and acceptor moieties, as well as the nature and length of the π-conjugated spacer.[3] Considerable progress has been made on design and synthesis of large β chromphores with new electron acceptor groups, such as 4,5,5 -trimethyl-2,5-dihydrofuran (TCF) derivatives,[4, 5] 1,3-diethyl-2-thiobarbituri cacid,[6, 7] 1,3-bis(dicyanomethylidene)indane,[8, 9] 3-(dicyanomethylidenyl)-2,3-dihydrobenzothiophene-2-ylidenyl-1,1-dioxide.[10] However, its counterpart electron donor groups are relatively less investigated in the newest generation of EO chromophores, the commonly used electron donor groups are still triarylamines,[11] *N, N* -dialkylaryl amines,[12] 1,3-dithiole,[13-15] 4H -Pyran-4-ylidene[16] and incorporation of these electron donor groups in NLO chromophores were observed saturate molecular nonlinearity. Thus, it is necessary to modify the electron donor groups carefully so that the full potential of organic chromophore EO activity can be realized.



Scheme 1 Molecular structures of A and B.

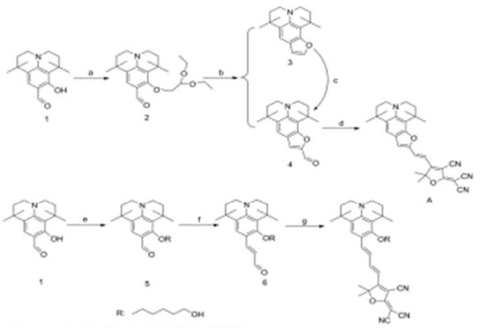
Theoretical and experimental studies have shown that, upon introduction heteroaromatic rings in chromophores can significantly enhance the molecular hyperpolarizability. This enhancement can be ascribed to low delocalization energy of heteroaromatic rings, and its electron rich/poor characteristic can act as an auxiliary donor/auxiliary acceptor.[17-20] Of the heterocyclic rings studied in NLO chromophores, it should be noted that most of them are single rings (such as thiophene, pyrrole, furan and thiazole),[19, 21, 22] benzo-fused five-membered heterocyclic rings have received little consideration.[23, 24] Driven by this consideration, we started a general investigation of benzo-fused five-membered heterocyclic rings which suitable for building NLO chromohores. Benzo[b]furan is an interesting heterocyclic with some distinctive characteristics which is suitable for constructing NLO chromophores. a) The two fused ring provide a planar geometry allows effective intramolecular charge transfer. b) The lone pair electron of oxygen atom in the ring can conjugate with the π-conjugated systems that enhance the density of electronic cloud at the donor end. Benzo[b]furan has been investigated in dye-sensitized solar cells (DSSCs) and exhibited a good solar-to-electric conversion.[25] In the field of NLO chromophores, to the best of our knowledge, only two papers report incorporate benzo[b]furan ring as the electron donor.[26, 27] However, the potential application of benzo[b]furan ring in NLO chromophors is not fully explored. It has been experimentally demonstrated that julolidinyl is an efficient donor group in the new NLO chromophores for it has more efficient p-π conjugate of the amino atom with the phenyl ring than triarylamines, *N, N* -dialkylaryl amines.[12, 28] We expected that further enhancement of molecular hyperpolarizablity of dipolar choromophores can be achieved by combining these two parts.

In this regard, we have designed and synthesized chromophores A which 1,1,7,7-Tetramethyljulolidine fused furan ring as the electron donor, 2-(3-cyano-4,5,5-trimethyl-5H-furan-2-ylidene)-maloni-trile (TCF) as the electron acceptor bridged by an ene unit. 1,1,7,7-Tetramethyljulolidine donor containing Chromophore B was chosen as a reference compound for comparison. Compared with other typical push-pull dipolar chromophores using aniline analogues as electron donors, and the heterocyclic rings are usually located in the π-bridge, in our new chromophore A, the heterocyclic furan ring is fused with strong electron donor group-julolidine, these two parts are combined as electron donor. Thus, the benzo[b]furan ring is introduced at the donor end. The influence of the benzo[b]furan ring on the linear and nonlinear optical properties of the new chromophore have been carefully studied. Compared with chromophore B, benzo[b]furan-containing chromophore A showed an enhanced EO activity and might represent the new type NLO chromophore that may be suitable for EO materials and devices application.

Results and discussion

Synthesis of chromophores

The chromophores A and B were obtained as the scheme 2. The derivative 2 was prepared by a substitution reaction of commercially available 1 with bromoacetaldehyde diethyl acetal.[25] After the ring closure reaction of 2, compound 3 and aldehyde 4 were prepared. Aldehyde 4 can also be obtained by Vilsmeier reaction with compound 3 in the presence of $POCl_3$ and DMF. The derivative 5 was obtained by substituting of 1 with 1-Chloro-6-hydroxyhexane, Compound 5 was then treated with tributyl(1,3-dioxolan-2-ylmethyl)phosphonium bromide to obtain, after aqueous acidic workup, compound 6.[29] Finally, chromophores A and B were obtained by Knoevenagel condensation of aldehyde 4, 6 and the TCF in yield 83 %, 73 % respectively.



(a) bromoacetaldhyde diethylacetal, K_2CO_3, DMF, N_2, 160 °C, 24h.
(b) CF_3COOH, THF, H_2O, rt, 2h.
(c) DMF, $POCl_3$,0 °C to rt, 2h.
(d) ethanol, TCF, piperidine, reflux, 4h.
(e) 6-Chlorohexanol, K_2CO_3, DMF, N_2, 120 °C, 12h.
(f) i. tributyl(1,3-dioxolan-2-ylmethyl)phospho-nium bromide, NaH, cat. 18-crown-6, THF, rt, 20 h; ii. HCl (10%), THF, rt, 1 h.
(g) ethanol, TCF, piperidine, reflux, 2h.

Scheme 2 Synthetic scheme for chromophores A and B.

To understanding the role of the benzo[b]furan on the properties of these NLO chromophores, DFT calculations have been carried out on chromophores A and B using B3LYP/6-311G** geometries by means of Gaussian 03 (G03). All C-C double bonds outside the aromatic rings were set to be in trans configuration and their geometries were optimized in vacuum. Based on the previous optimized geometries, we also carried TD-DFT calculations on chromophores A and B. The results showed that the lowest energy transitions of two chromophores are based on the HOMO-LUMO orbitals, which are corresponding to their maximum absorptions, the related dates are listed in table S1. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) from the calculation of chromophores A and B are depicted in Figure S1. It could be clearly observed that electron density asymmetry distribute along the dipolar axis of the chromophores. At the HOMO state, the electron density is concentrated on the donor moiety, and the density in LUMO on the π-bridge and acceptor moiety. Here, the energy of the HOMO, LUMO levels, Zero-frequency (static) molecular first hyperpolarizability (β_0) and dipole moment (μ) of A and B are listed in Table 1. On passing from A to B there is a shift of the HOMO energies towards a higher state by 0.02 eV, and a shift of the LUMO energies towards a lower state by 0.12 eV, indicating that the introduction of the benzo[b]furan ring of chromophore A influences of the LUMO energy to a greater extent than the HOMO energy. Both factors resulted in a smaller energy gap of chromophore A ($E_{ge} = 2.23$ eV) than chromophore B ($E_{ge} = 2.33$ eV). By using the "two level model",[30] β values is associated with the energy gap between HOMO and LUMO, a lower gap of chromophore

Table 1 Electrochemical[a] and DFT Calculated[b] properties of chromophores A and B

	Cyclic voltammetry[a]			DFT calculations[b]				
chromophore	E_{ox}/V	E_{red}/V	E_{ge}/ eV	μ/ D	β_0/ 10^{-30} esu	HOMO/ eV	LUMO/ eV	E_{ge}/ eV
A	0.61	-0.53	1.14	18.7	262	-5.54	-3.31	2.23
B	0.64	-0.64	1.28	21.2	294	-5.52	-3.19	2.33

[a] 10^{-3} M in CH_2Cl_2 versus Ag/AgCl, glassy carbon working electrode, Pt counter electrode, 20°C, 0.1M Bu_4NPF_6,100 mv s^{-1} scan rate, Ferrocene internal reference E1/2 = +0.43 V.

[b] DFT calculations at the B3LYP6-311G** level in vacuum.

A indicates the π-electron delocalization efficiency and may get a larger β. However, the calculated β_0 of the corresponding chromophores fail to follow such a principle, is 262 $\times 10^{-30}$ esu for A, which is smaller than B (294 $\times 10^{-30}$ esu). The phenomenon is reasonable if we consider the polyene is the most effective π-conjugated bridges for large β.[5] Chromophore A just has one vinyl bridge outside the aromatic rings, while chromophore B has two.

The electrochemical properties of chromophores A and B were studied by cyclic voltammetry (CV). As shown in Fig. 1. Both chromophores show a similar trend having an irreversible reduction wave corresponding to the acceptor moieties at $E_{\rm red}$ = -0.53 V and -0.64 V (vs Ag/AgCl) for A and B, respectively. Chromophore A showed two oxidation waves, the first one is a reversible wave with half-wave potentials $E_{1/2} = 0.5(E_{ox}+E_{red})$ at about 0.61 V corresponding to the 1,1,7,7-Tetramethyljulolidine fused furan donor group. And for chromophore B, one irreversible oxidation wave was observed, where the half-wave oxidation potential $E_{1/2}$ was determined to be 0.64 V. The results are summarized in Table 1. In comparison with chromophore B, the introduction of benzo[b]furan ring of chromophore A give rise to a decrease of E_{ox} and ∣E_{red}∣ values. The easier oxidation and reduction process of chromophore A means a weaker interaction between the donor and acceptor end groups. For the same acceptor, the decrease in ∣$E_{\rm red}$∣ is more noticeable than the energy in $E_{\rm ox}$. The observed trends are also confirmed by computational calculations, which show that the $E_{\rm LUMO}$ values decrease with the introduction of the benzo[b]furan ring. Concerning the electronchemical bandgap, chromophore A (1.14 eV) has a lower energy gap than chromophore B (1.28 eV) by 0.14 eV, in agreement with the previous bandgap calculations, thus suggesting the excellent intramolecular charge transfer (ICT) and larger β values of chromophore A.

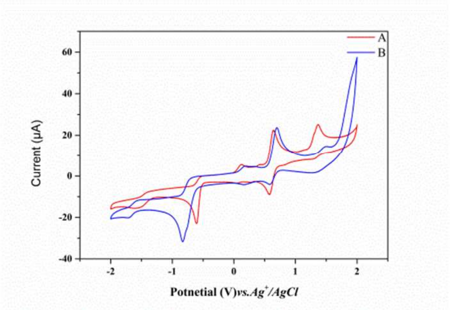


Fig. 1 Cyclic voltammograms of chromophores A and B.

The UV-vis spectral absorption of the two chromophores recorded in a series solvents with different dielectric constants are displayed in Figure 2 and the relevant parameters are compiled in Table 2. The two chromophores exhibited the similar typical π-π* intramolecular charge-transfer (ICT) band spectrum and the absorption maximum ($\lambda_{\max}$) is significantly depends on the solvent polarity. Increasing the solvent polarity from 1,4-dioxane to dichloromethane causes a clear red shift of the $\lambda_{\max}$ and the absorption bands shape changes from broad to sharp gradually. Both of these results properly means chromophores A and B possess neutral ground state (in 1,4-dioxane and toluene) and then approaching the cyanine limit (in dichloromethane and chloroform).[31] Compared with chromophore B with a $\lambda_{\max}$ of 624 nm in 1,4-dioxane and 636 nm in toluene, the $\lambda_{\max}$ of chromophore A with an additional furan ring at the donor end red-shifted by 26 nm to 650 nm in 1,4-dioxane and by 34 nm to 670 nm in toluene, respectively. These facts reflect a lower energy gap of chromophore A than chromophore B, in agreement with the cyclic voltammetry and theoretical calculations discussed above. It is widely recognized that low energy bands in UV-vis spectra indicating a correlated enhancement of π-electron delocalization and large β. The $\lambda_{\max}$ for the chromophore A and that of the chromophore B appear the same values at 711 nm in chloroform and 714 nm in dichloromethane, thereby suggesting their comparable ICT abilities in such dielectric environment.

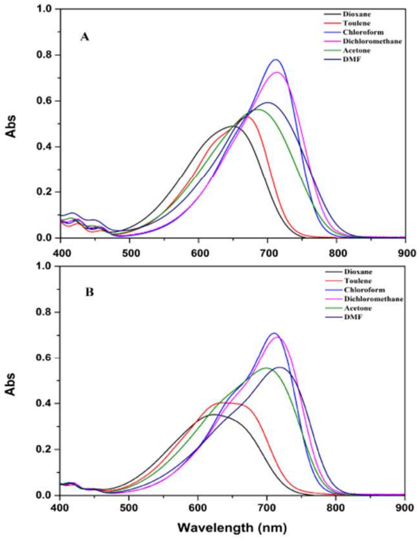


Fig. 2 Photophysical spectral of chromophores A and B in different solvents.

In more polar solvents like acetone, both chromophores reversed to a blue shift of λ_{max} and accompanied by a change of absorption bands from sharp to broad. A possible explanation for this behaviour was that both chromophores can be polarized beyond into the zwitterionic ground state in more polar solvents.[31, 32] In addition, chromophore A is more blue-shifted than chrmophore B by comparison of their λ_{max} values in acetone. Thus, we can speculate that chromophore A is more zwitterionic than chromophore B.[33] A further increase of solvents polarity causes again the red shift of λ_{max} of 14 nm and 20 nm from acetone to DMF, respectively. These interesting solvatochromism behaviors of chromophores A and B was ascribed to the use of strong julolidine-based electron donor, as is usually the case for julolidine derivatives.[12] Notably, the inclusion of an additional furan ring at the donor end of chromophore A causes an enhanced ground-state polarization.

Table 2 Photophysical properties of A and B

Entry	Solvent	λmax/ nm	ε/ 104 M-1 cm-1	FWHM/ nm
A	Dioxane	650	1.63	128
	Toulene	670	1.77	116
	Chloroform	711	2.59	107
	Dichloromethane	714	2.42	118
	Acetone	686	1.87	147
	DMF	700	1.98	147
B	Dioxane	624	3.51	145
	Toulene	636	4.03	141
	Chloroform	711	7.09	114
	Dichloromethane	714	6.92	121
	Acetone	699	5.54	154
	DMF	719	5.58	143

Absorption spectra were measured in 10^{-5} M solutions

The thermal stabilities of chromophores A and B were investigated by thermogravimetric analysis (TGA). The decomposition temperature (T_d, temperature at which 5 % mass loss occurs during heating), as shown in Figure S2. Both A and B displays good thermal stability with the onset decomposition temperature over 225 °C. Compared with chromophore B (239°C), benzo[b]furan containing chromophore A (229 °C) showed no obvious reduce decomposition temperature, which suggests that both chromophores appear to be promising for materials working and processing. To investigate the macroscopic EO activity of the new chromophores A or B were doped into amorphous polycarbonate (APC) by a loading density of 20 wt%. The films were prepared by spin coating on the indium tin oxide (ITO) glass substrate. The EO activities of the poled films were measured by the Teng-Man method at a wavelength of 1310 nm. The poled films containing A showed a maximum EO coefficient (r_{33}) of 52 pm/V, which represents a nearly 48% improvement over chromophore B with a maximum r_{33} values of 35 pm/V. Such a great improvement in r_{33} of A might be attributed to that fused benzo group provides a more planar geometry, which makes an effective intramolecular charge transfer. This result indicated that 1,1,7,7-Tetramethyljulolidine fused furan ring derived chromophores provide a new generation EO materials.

Conclusions

Two novel of TCF based NLO chromophores with different electron donor structures have been synthesized. Chromophore A having 1,1,7,7-Tetramethyljulolidine fused furan as the electron donor group, while chromophore B only contain 1,1,7,7-Tetramethyljulolidine at the donor end for comparison. Theoretical and experimental investigations suggest that benzo[b]furan group play a critical role in affecting the linear and nonlinear properties of dipolar chromophores. In general, the energy gap of chromophore B is 1.28 eV, the introduction of benzo[b]furan into the chromophore A leads to a reduced energy gap at 1.14 eV. As mentioned above, a lower energy gap may lead to larger β. From linear properties of chromophores A and B determined in different polarity solvents, it is evident that both chromophores can be polarized efficiently and got a maximum absorption more than 710 nm. In contrast with chromophore B, chromophore A can be polarized more easily. In addition, chromophore A showed a maximum EO coefficient of 52 pm/V, which is nearly 48% improvement of EO coefficient (r_{33}) over chromophore B (35 pm/V) due to the introduction of benzo[b]furan ring at the donor end. These two chromophores showed excellent thermal stability with the onset decomposition temperatures higher than 229 °C. This work demonstrates a promising way to developing new NLO chromophores offering enhanced EO activities that may be suitable for EO materials and devices application.

Experimental details

Instruments and materials

^{1}H NMR and ^{13}C NMR spectra were determined by an Advance Bruker 400M (400MHz) NMR spectrometer (tetramethylsilane as internal-reference). The MS spectra were obtained on MALDI-TOF (Matrix Assisted Laser Desorption/Ionization of Flight) on BIFLEXIII (Broker Inc.) spectrometer. The UV-vis experiments were performed on Cary 5000 photo spectrometer. The TGA was determined by TA5000-2950TGA (TA co) with a heating rate of 10 °C min^{-1} under the protection of nitrogen. Cyclic voltammetry (CV) experiments were performed on a CHI660C electrochemical workstation by a cyclic voltammetry (CV) technique in CH_2Cl_2 solution, using glassy carbon as working electrode, Pt as counter electrode, Ag/AgCl electrode as the reference electrode in the presence of 1 mM n-tetrabutylammonium perchlorate as the supporting electrolyte. The DFT calculations using Gaussian 03 were carried out at the hybrid B3LYP level by employing the split valence 6-31 g (d, p) basis set.[34] All chemicals, commercially available, are used without further purification unless stated. The DMF and $POCl_3$ were freshly distilled prior to its use. 2-dicyanomethylene-3-cyano-4-methyl-2, 5-dihydrofuran (TCF) acceptor was prepared according to the literature.[35]

Poling and r_{33} measurements

Guest–host polymers were prepared by formulating chromophores A and B into amorphous polycarbonate (APC) using dibromomethane (CH_2Br_2) as the solvent. The resulting solutions were filtered through a 0.22 µm Teflon membrane filter and spin-coated onto indium tin oxide (ITO) glass substrates. Films of doped polymers were baked in a vacuum oven at 40ºC to remove the residual solvent. The poling process was carried out at a temperature of T_g of the polymer. The r_{33} values were measured using Teng-Man simple reflection technique at the wavelength of 1310 nm. [36]

Synthesis

Compound 2: Under N_2 atmosphere to a solution of 8-hydroxy-1,1,7,7-tetramethyl-formyljulolidine 1 (6 g, 22 mmol), K_2CO_3 (6 g, 43 mmol), and bromoacetaldhyde diethylacetal (4.2 g, 22 mmol) in DMF (50 mL) was heated at 160 °C for 24 h. DMF was removed under reduced pressure. The crude product was redissolved in 200ml water and extracted with ethyl acetate (3 × 50 ml). The combined organic layer was collected and dried with anhydrous $MgSO_4$. The organic layer was removed in vacuo. The residue was purified by column chromatography (acetone: Petroleum ether = 1:100, v/v) to give a brown solid 2 (5.6 g, 14 mmol) in 65.4 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): δ 9.97 (s, 1H), 7.55 (s, 1H), 4.96 – 4.90 (m, 1H), 4.00 (d, J = 5.1 Hz, 2H), 3.80 (dq, J = 14.1, 7.0 Hz, 2H), 3.66 (dq, J = 14.1, 7.0 Hz, 2H), 3.35 – 3.26 (m, 2H), 3.26 – 3.20 (m, 2H), 1.71 (dd, J = 12.0, 5.9 Hz, 4H), 1.46 (s, 6H), 1.26 (dd, J = 9.4, 4.6 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$, δ ppm): δ 188.07 (s), 160.89 (s), 148.25 (s), 126.67 (s), 126.26 (s), 121.21 (s), 117.05 (s), 101.61 (s), 78.18 (s), 63.45 (s), 47.61 (s), 46.98 (s), 39.54 (s), 35.77 (s), 32.67 (s), 32.17 (s), 30.32 (s), 29.77 (s), 15.47 (s). MS (EI): m/z 389.2598 ($C_{23}H_{35}NO_4$, calcd: 389.53).

Compound 3 and 4: THF and water was added to a flask containing 2 (2.4 g, 6.2 mmol). Then, TFA(10 ml) was added to the solution. After stirred at room temperature for 4h, the mixture was poured into saturated aqueous $NaHCO_3$.The organic layers were extracted with ethyl acetate (3×50ml). The combined extracts were dried with anhydrous $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by column chromatography (acetone: Petroleum ether = 1:150, v/v) to give **3** (1 g, 3.7 mmol) as a yellow oil liquid in 60.3% yield and **4** (0.17 g, 0.4 mmol, acetone: Petroleum ether = 1:50, v/v) as a yellow solid in 9.3% yield.

Compound 4 can also be obtained as follows: To a solution of 3 (0.4 g, 1.5 mmol) and DMF (0.22 g, 2.9 mmol) at 0 °C was added $POCl_3$ (0.17 ml, 1.8 ml) by dropwise. After stirred at room temperature for 3h.The mixture was poured into saturated aqueous $NaHCO_3$. The organic layers were extracted with ethyl acetate (3×50ml). The combined extracts were dried with anhydrous $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by column chromatography to give a yellow solid 4 (0.4 g, 1.3 mmol) in 90.6% yield.

Compound 3: ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): δ 7.41 (d, J = 2.2 Hz, 1H), 7.27 (s, 1H), 6.56 (d, J = 2.2 Hz, 1H), 3.15 – 3.06 (m, 4H), 1.91 – 1.78 (m, 4H), 1.53 (s, 6H), 1.34 (s, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.27 (s), 141.87 (s), 116.59 (s), 105.99 (s), 47.86 (d, J = 8.0 Hz), 39.44 (s), 37.56 (s), 32.97 (s), 32.58 (s), 32.21 (s), 29.77 (s). MS (EI): m/z 269.1656 ($C_{18}H_{23}NO$, calcd: 269.38).

Compound 4: ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): δ 9.61 (s, 1H), 7.34 (s, 2H), 3.28 – 3.20 (m, 4H), 1.86 – 1.75 (m, 4H), 1.54 (s, 6H), 1.32 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, δ ppm): δ 177.58 (s), 155.86 (s), 150.95 (s), 143.66 (s), 130.94 (s), 118.23 (s), 116.96 (s), 112.54 (s), 47.36 (d, J = 2.5 Hz), 38.41 (s), 36.28 (s), 32.86 (s), 31.93 (s), 31.20 (s), 29.39 (s). MS (EI): m/z 297.1753 ($C_{19}H_{23}NO_2$, calcd: 297.39).

Chromophore A: A solution of 4 (0.2 g, 0.68 mmol) and TCF (0.21 g, 1 mmol) in 50ml ethanol. Two drops of Piperidine was added and refluxed for 4h, then cooled to room temperature. After removal of the solvent in vacuo, the residue was purified by column chromatography (acetone: Petroleum ether = 1:5, v/v) to give a green solid 5 (0.27 g, 0.56 mmol) in 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): δ 7.53 (d, J = 15.2 Hz, 1H), 7.28 (s, 1H), 7.12 (s, 1H), 6.67 (d, J = 15.2 Hz, 1H), 3.40 – 3.28 (m, 4H), 1.88 – 1.83 (m, 2H), 1.81 – 1.75 (m, 2H), 1.72 (s, 6H), 1.54 (s, 6H), 1.32 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, δ ppm): δ 176.36 (s), 172.01 (s), 156.97 (s), 150.01 (s), 144.87 (s), 131.69 (s), 119.74 – 119.54 (m), 117.97 (s), 112.96 (s), 112.10 (s), 111.82 (s), 111.36 (s), 108.77 (s), 96.51 (s), 47.49 (d, J = 5.1 Hz), 37.71 (s), 35.60 (s), 32.73 (s), 31.71 (s), 30.44 (s), 29.70 (s), 29.05 (s), 26.61 (s). MS (MALDI-TOF): m/z 478.104 ($C_{30}H_{30}N_4O_2$, calcd: 478.58). Anal. Calcd for $C_{30}H_{30}N_4O_2$: C, 75.29; H, 6.32; N, 11.71. Found: C, 75.25; H, 6.40; N, 11.74.

Compound 5: Under N_2 atmosphere to a solution of 8-hydroxy-1,1,7,7-tetramethyl-formyljulolidine (2.5 g, 10 mmol) in anhydrous DMF was added 6-Chlorohexanol (1.88 g, 13 mmol) and K_2CO_3 (1.89 g, 13 mmol). The mixture was stirred at the temperature of 100 °C for 12 h and then poured into ice water. The organic layers were extracted with ethyl acetate (3×50 ml). The combined organic extracts were dried over $MgSO_4$. After the removal of the solvent, the residue was purified by column chromatography using hexane and acetone as eluent to give a yellow solids 5 (2.32 g, 6.2 mmol) in 67.4 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): δ 9.92 (s, 1H), 7.57 (s, 1H), 3.96 (t, 2H), 3.66 (t, 2H), 3.29 (t, J = 5.9 Hz, 2H), 3.25 – 3.20 (m, 2H), 2.02 (s, 1H), 1.89 (m, 2H), 1.76 – 1.66 (t, 4H), 1.61 (d, J = 6.6 Hz, 2H), 1.55 – 1.44 (m, 4H), 1.42 (s, 6H), 1.26 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, δ ppm): δ 187.83 (s), 162.08 (s), 148.38 (s), 126.09 (s), 125.52 (s), 120.73 (s), 117.03 (s), 78.60 (s), 62.44 (s), 47.46 (s), 46.81 (s), 39.34 (s), 35.62 (s), 32.63 (s), 32.43 (s), 32.02 (s), 30.22 (s), 30.00 (s), 29.73 (s), 25.76 (d, J = 4.5 Hz). MS (MALDI-TOF): m/z 372.685 ($C_{23}H_{35}NO_3$, calcd: 373.53).

Compound 6: To a solution of 1 (0.55 g, 1.5 mmol) and tributyl(1,3-dioxolan-2-ylmethyl)phosphonium bromide (1.2 g, 3.3 mmol) in anhydrous THF was added a sodium hydride (0.1 g, 4.5 mmol), 18-crown-6 as the catalyst. After the mixture was stirred at room temperature for 20 h, HCl/THF (v/v) solution was added to quenching the reaction and kept to stir for another 1 h. Then, the organic layers were extracted with ethyl acetate (3×50ml). The combined organic extracts were dried over $MgSO_4$. After the removal of the solvent, the residue was purified by column chromatography (acetone: Petroleum ether = 1: 20, v/v) to give yellow oils 6 (0.38 g, 0.95 mmol) in 63.5% yield. ^1H NMR (400 MHz, $CDCl_3$, δ ppm): δ 9.55 (s, 1H), 7.60 (d, J = 15.6 Hz, 1H), 7.32 (s, 1H), 6.53 (dd, J = 15.6, 8.0 Hz, 1H), 3.82 (t, J = 6.8 Hz, 2H), 3.67 (t, J = 6.5 Hz, 2H), 3.31 – 3.24 (m, 2H), 3.24 – 3.16 (m, 2H), 1.94 – 1.84 (m, 2H), 1.72 (dd, J = 10.6, 5.0 Hz, 4H), 1.67 – 1.60 (m, 2H), 1.59 – 1.44 (m, 4H), 1.42 (s, 6H), 1.26 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, δ ppm): δ 193.96 (s), 158.42 (s), 150.50 (s), 146.21 (s), 126.61 (s), 124.09 (s), 122.73 (s), 121.86 (s), 114.51 (s), 62.69 (s), 47.38 (s), 46.79 (s), 39.59 (s), 35.90 (s), 32.61 (d, J = 8.2 Hz), 32.10 (s), 30.49 (s), 29.97 (d, J = 16.6 Hz), 25.83 (d, J = 13.8 Hz). MS (EI): m/z 399.2929 ($C_{25}H_{37}NO_3$, calcd: 399.57).

Chromophore B: A solution of 6 (0.15 g, 0.38 mmol) and TCF (0.06 g, 0.45 mmol) in 50ml ethanol was refluxed for 2h, then cooled to room temperature. After removal of the solvent in vacuo, the residue was purified by column chromatography (acetone: Petroleum ether = 1: 6, v/v) to give dark solid B (0.16 g, 0.28 mmol) in 73 % yield. ^1H NMR (400 MHz, $CDCl_3$, δ ppm): δ 7.79 – 7.69 (m, 1H), 7.35 (t, J = 7.3 Hz, 2H), 6.86 (dd, J = 14.7, 11.5 Hz, 1H), 6.27 (d, J = 14.8 Hz, 1H), 3.82 (t, J = 6.7 Hz, 2H), 3.67 (t, J = 6.5 Hz, 2H), 3.37 (t, J = 6.1 Hz, 2H), 3.32 – 3.26 (m, 2H), 1.95 – 1.86 (m, 2H), 1.74 (t, J = 5.9 Hz, 4H), 1.68 (s, 6H), 1.66 – 1.61 (m, 2H), 1.56 (dd, J = 15.2, 7.4 Hz, 2H), 1.49 (dd, J = 14.7, 8.0 Hz, 2H), 1.42 (s, 6H), 1.30 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, δ ppm): δ 176.64 (s), 172.95 (s), 159.62 (s), 151.18 (s), 147.53 (s), 145.95 (s), 127.55 (s), 124.50 (s), 122.42 (s), 122.06 (s), 116.63 (s), 113.23 (s), 112.78 (s), 112.35 (d, J = 7.2 Hz), 96.41 (s), 62.66 (s), 47.74 (s), 47.11 (s), 39.12 (s), 35.40 (s), 32.55 (d, J = 5.3 Hz), 32.08 (s), 30.04 (d, J = 3.9 Hz), 29.53 (s), 26.60 (s), 25.93 (s), 25.71 (s). MS (MALDI-TOF): m/z 580.139 ($C_{36}H_{44}N_4O_3$, calcd: 580.76). Anal. Calcd for $C_{36}H_{44}N_4O_3$: C, 74.45; H, 7.64; N, 9.65. Found: C, 74.55; H, 7.69; N, 7.67.

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Notes and references

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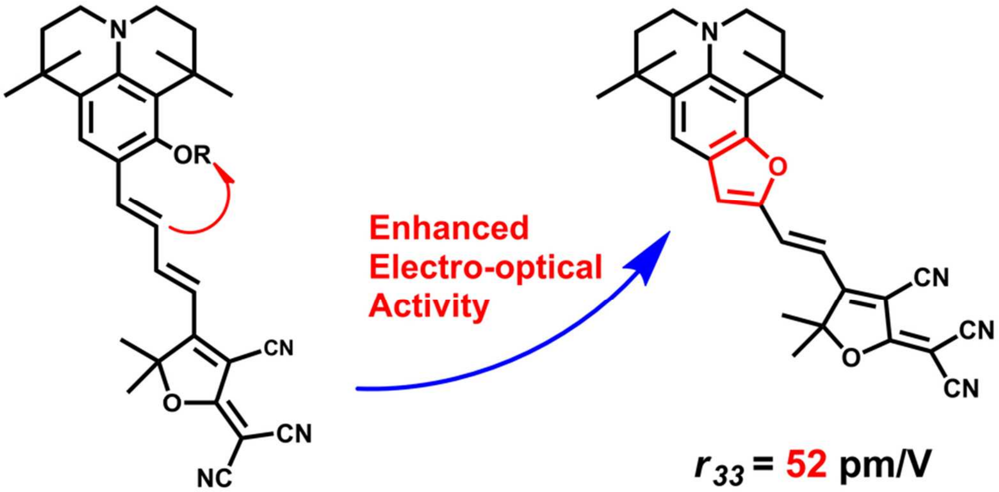

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