Preparation and Photophysical Properties of All-*trans* Acceptor- π -Donor (Acceptor) Compounds Possessing Obvious Solvatochromic Effects

Yu-Lu Pan,^A Zhi-Bin Cai,^{A,C} Li Bai,^A Sheng-Li Li,^B and Yu-Peng Tian^B

^ACollege of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, China.

^BDepartment of Chemistry, Anhui Province Key Laboratory of Functional

Inorganic Materials, Anhui University, Hefei 230039, China.

^CCorresponding author. Email: caizbmail@126.com

A series of all-*trans* acceptor– π -donor (acceptor) compounds (**BAQ**, **SFQ**, **BLQ**, and **XJQ**) were conveniently synthesised and characterised by infrared, nuclear magnetic resonance, mass spectrometry, and elemental analysis. Their photophysical properties, including linear absorption, one-photon excited fluorescence, two-photon absorption, and two-photon excited fluorescence, were systematically investigated. All the compounds show obvious solvatochromic effects, such as significant bathochromic shifts of the emission spectra and larger Stokes shifts in more polar solvents. Under excitation from a femtosecond Ti : sapphire laser with a pulse width of 140 fs, they all exhibit strong two-photon excited fluorescence, and the two-photon absorption cross-sections in THF are 851 (**BAQ**), 216 (**SFQ**), 561 (**BLQ**), and 447 (**XJQ**) GM respectively. A combination of density functional theory (DFT) and time-dependent density functional theory (TDDFT) approaches was used to investigate the relationships between the structures and the photophysical properties of these compounds. The results show that they may have a potential application as polarity-sensitive two-photon fluorescent probes.

Manuscript received: 9 January 2017. Manuscript accepted: 24 April 2017. Published online: 24 May 2017.

Introduction

Two-photon absorption (TPA), which is defined as the simultaneous absorption of a pair of photons during the excitation of a molecule, was first predicted by Göppert-Mayer.^[1] Molecules with large TPA cross-sections (σ) have potential significant applications in many fields, such as two-photon fluorescence microscopy,^[2,3] optical limiting,^[4-6] three-dimensional optical data storage,^[7–9] and photodynamic therapy.^[10–12] Recently, two-photon fluorescent (TPF) probes have attracted considerable interest because of their high spatial resolution, deep penetration, low photodamage, low phototoxicity, and reduced photobleaching.^[13–15] Conventional fluorescent molecules such as rhodamine, fluorescein, and cyanine dyes usually exhibit a small σ (σ < 100 GM; 1 GM = 1 × 10⁻⁵⁰ cm⁴ s photon⁻¹), which restricts their application as TPF probes. Thus, the development of efficient fluorescent molecules with a large σ is clearly necessary.

Considering their practical applications as probes, the design of new TPA materials must combine enhanced σ with a high fluorescence quantum yield (Φ) and low excitation energy to decrease photodamage. Herein, we selected styrene as the π -bridge, triphenylamine (or 1-methylpyrrole, or thiophene) as the electron donor (D) and the formyl (or nitro) as the electron acceptor (A) to design four all-*trans* A- π -D (or A- π -A') compounds (**BAQ**, **SFQ**, **BLQ**, and **XJQ**) (Fig. 1). Styrene is a good

Journal compilation © CSIRO 2017

electron-transport channel, which can greatly facilitate the charge transfer between the donor and the acceptor.^[16,17] Increasing the number of styrene moieties and the transconfiguration of the carbon-carbon double bond may improve the quantum efficiency of the $\pi^*-\pi$ electronic transition, and thus enhance the fluorescence emission.^[18,19] Triphenylamine has special propeller starburst molecular structure; pyrrole and thiophene are closed circular 6π -electron conjugated systems. Owing to their high electron-donating ability, electrochemical activity, and environmental stability, they have been widely used in opto- and electro-active materials.^[20-24] The formyl group consists of a carbonyl group joined by a single bond to a hydrogen atom, which is rarely chosen as the electron acceptor in TPA materials. However, we have previously reported the TPA behaviour of a series of new compounds with a formyl group.^[25,26] The results reveal that formyl has a correspondingly strong electron-withdrawing ability and is beneficial in intramolecular charge transfer (ICT).

The four target compounds are all-*trans* conjugated aromatic aldehydes. These kinds of compounds are usually synthesised using fairly complicated routes including six to nine reaction steps.^[27–32] The routes are so long that they significantly decrease overall efficiency. In the present paper, a simple, mild, and efficient three-step synthetic method has been adopted, which comprises the following reactions: Arbuzov reaction, solvent-free



Fig. 1. Molecular structures of the target compounds BAQ, SFQ, BLQ, and XJQ.

Horner–Wadsworth–Emmons (HWE) reaction, and Mizoroki– Heck reaction. Both the yield and the *trans*-stereoselectivity are satisfactory.

These target compounds were fully characterised and gave well-defined NMR, IR, and mass spectrometry spectra corresponding to their expected molecular structures. Their linear and non-linear photophysical properties were systematically investigated in various solvents. The experimental studies of the compounds were computationally supplemented by density functional theory (DFT) and time-dependent density functional theory (TDDFT) to provide deep insight into their structure– property relationships. Interestingly, it was found that all the compounds investigated exhibit pronounced positive polarity-dependent solvatochromic effects and correspondingly large σ values. Therefore, their potential application as polarity-sensitive TPF probes can be proposed.

Results and Discussion

Synthesis and Characterisation

Among the four target compounds, **BLQ**, **SFQ**, and **XJQ** are new. **BAQ** was synthesised by McNulty^[31] and Dubinina^[32] using a seven-step or nine-step synthetic route where Wittig reaction was repeatedly used. Herein, we presented a three-step method to readily prepare the target compounds in moderate yields. The synthetic routes are depicted in Scheme 1.

[(4-Ethenylphenyl)methyl]phosphonic acid diethyl ester (LSZ) was obtained by Arbuzov reaction of 4-(chloromethyl)

styrene with triethyl phosphite. Then, **LSZ** was subjected to the solvent-free HWE reaction with different aromatic aldehydes to furnish the desired *trans*-alkenes **3a–3d**. The HWE reaction is the reaction of stabilised phosphonate carbanions with carbonyl compounds to produce predominantly *trans*-alkenes. Herein, more attention has been paid to the HWE reaction under solvent-free conditions instead of in organic solvents owing to its environmental and economic benefits. Finally, the target compounds **BAQ**, **SFQ**, **BLQ**, and **XJQ** were synthesised from **3a–3d** via the Mizoroki–Heck reaction. The Mizoroki–Heck reaction has been proved to be a powerful method for C=C bond formation in organic synthesis.

In the ¹H NMR spectra, the chemical shifts (δ) of **3a–3d** at 6.72–6.77 ppm (J₁ 17.6–17.7, J₂ 10.9–11.1 Hz, 1H), 5.76– 5.91 ppm (J 17.5–17.9 Hz, 1H), and 5.24–5.32 ppm (J 10.8– 11.3 Hz, 1H) correspond to the hydrogens attached to the terminal carbon-carbon double bonds. Doublets with coupling constants of J = 16.1 - 16.5 Hz were observed for the target compounds, which is consistent with the expected all-trans configurations. The peaks at 9.98-10.00 ppm are characteristic of the formyl groups. In the Fourier-transform (FT)-IR spectra, the strong bands between 1692 and 1697 cm⁻¹ were assigned to the stretching vibration of the carbonyl group. The characteristic absorption peaks at \sim 1587–1595 and 957–965 cm⁻¹ indicate the presence of the trans configuration at the carbon-carbon double bonds. Mass spectrometry was used to further verify the structures of the target compounds. The measured values $(m/z [M + H]^+ 478.1, 317.2,$ 314.3, 356.4) agree well with calculated ones.

Linear Absorption and TDDFT Computational Studies

The optical characteristics of the target compounds **BAQ**, **SFQ**, **BLQ**, and **XJQ** in solvents with different polarities are summarised in Table 1. The corresponding linear absorption spectra are shown in Fig. 2.

As depicted in Fig. 2, one can see that XJQ exhibits one absorption band, BAQ and SFQ show two obvious absorption bands, whereas one of the two absorption bands of BLQ degenerates into a shoulder. The high-energy bands centred at \sim 310 nm are attributed to the π - π * transition of the terminal electron donors (triphenylamine, thiophene, pyrrole). The lowenergy bands located at 376-412 nm originate from an ICT process. Their maximum absorption peaks (λ_{max}^{abs}) change slightly $(\leq 7 \text{ nm})$ with increase in solvent polarity from toluene (TOL) to CH₃CN, revealing that the surrounding solvent molecules have little influence on the transition energy of the target compounds. Compared with SFQ, BLQ, and XJQ, the λ_{max}^{abs} of BAQ is obviously red-shifted; this is due to the fact that the triphenylamine donor can significantly extend the π -conjugated system. The maximum molar absorption coefficients (ε_{max}) of the A- π -A' compound **XJQ** are larger than those of the A- π -D compounds (BAQ, SFQ, and BLQ), which implies that the nitro acceptor improves the light-absorbing ability of the entire molecule.

To further analyse the assignment of transitions in the absorption spectra, TDDFT calculations using *Gaussian 09* and B3LYP/6–31G* basis sets were performed on the target compounds. The compositions of some frontier orbitals are listed in Table S1 (Supplementary Material).

For **BAQ**, **SFQ**, and **BLQ**, the low-energy bands (calculated at 387, 390, and 417 nm) were assigned to the ICT transition due to HOMO \rightarrow LUMO. The high-energy bands (calculated at 321, 322, and 327 nm) mainly due to the HOMO \rightarrow LUMO + 1, HOMO \rightarrow LUMO + 1, and HOMO - 1 \rightarrow LUMO respectively



Scheme 1. Synthesis of the target compounds BAQ, SFQ, BLQ, and XJQ.

were assigned to the π - π * transition of triphenylamine (or thiophene, or pyrrole). In addition, **XJQ** exhibits one absorption band (calculated at 368 nm) originating from HOMO \rightarrow LUMO + 1, which corresponds to the ICT transition. Thus, the results from the theoretical calculations are consistent with their experimental absorption spectra.

One-Photon Excited Fluorescence and Solvatochromic Properties

The one-photon excited fluorescence (OPEF) spectra of the target compounds **BAQ**, **SFQ**, **BLQ**, and **XJQ** in different

solvents are shown in Fig. 3. Insets are the fluorescence photographs and chromaticity coordinates diagram. The corresponding data are listed in Table 1.

In comparison with the absorption spectra, the one-photon emission spectra display a strong solvatochromic response to solvent polarity. It can be clearly seen from Table 1 and Fig. 3 that the OPEF maxima (λ_{max}^{OPEF}) of the target compounds show remarkable bathochromic shifts as the solvent polarity increases following the order: TOL < THF < CH₂Cl₂ < CH₃CN. The solvatochromic behaviour is closely related to the terminal electron donor (or acceptor). From TOL to CH₃CN, the λ_{max}^{OPEF}

Compound	Solvent	λ_{\max}^{abs} [nm]	$10^{-4} \varepsilon^{\rm B} [\rm mol^{-1} L \rm cm^{-1}]$	$\lambda_{\max}^{\text{OPEF C}}$ [nm]	$\Delta v^{\rm D} [{\rm cm}^{-1}]$	ϕ^{E}	$\lambda_{\max}^{\text{TPEF F}}$ [nm]	$\sigma^{\rm G}$ [GM]
BAQ	Toluene	412	2.36	490	3864	0.55	525	545
	THF	407	2.25	550	6388	0.31	577	851
	CH_2Cl_2	410	1.76	566	6722	0.17		
	CH ₃ CN	406	2.85	570	7087	0.02		
SFQ	Toluene	383	2.71	465	4604	0.46	502	83
	THF	376	3.74	479	5719	0.27	518	216
	CH_2Cl_2	383	2.94	502	6189	0.23		
	CH ₃ CN	382	3.80	514	7722	0.16		
BLQ	Toluene	401	2.01	463	3339	0.33	525	309
	THF	404	4.63	547	6471	0.26	577	561
	CH_2Cl_2	401	2.59	562	7144	0.12		
	CH ₃ CN	397	3.38	567	7552	0.02		
XJQ	Toluene	389	3.79	479	4830	0.14	546	223
	THF	387	4.76	505	6037	0.18	554	447
	CH_2Cl_2	394	3.79	545	7032	0.15		
	CH ₃ CN	394	6.26	570	7836	0.03		

Table 1. Photophysical properties of the target compounds BAQ, SFQ, BLQ, and XJQ in different solvents

^AMaximum linear absorption wavelength, $c = 1 \times 10^{-5} \text{ mol } \text{L}^{-1}$.

^BMaximum molar absorption coefficient.

^CMaximum one-photon excited fluorescence wavelength, $c = 1 \times 10^{-6} \text{ mol L}^{-1}$.

^DStokes shift.

^EFluorescence quantum yield, measured using quinine sulfate in 0.5 mol L⁻¹ sulfuric acid as the standard ($\Phi = 0.546^{[33]}$).

The experimental error is estimated to be 10-15 %.

^FMaximum two-photon excited fluorescence wavelength, $c = 1 \times 10^{-3} \text{ mol L}^{-1}$.

 $^{\rm G}$ Two-photon absorption cross-section. The experimental error is estimated to be 10–15 %.



Fig. 2. Linear absorption spectra of the target compounds in different solvents with a concentration of $1 \times 10^{-5} \text{ mol } \text{L}^{-1}$: (a) **BAQ**; (b) **SFQ**; (c) **BLQ**; and (d) **XJQ**.



Fig. 3. One-photon excited fluorescence spectra of the target compounds in different solvents with a concentration of 1×10^{-6} mol L⁻¹: (a) **BAQ**; (b) **SFQ**; (c) **BLQ**; and (d) **XJQ**. Insets are the fluorescence photographs and chromaticity coordinate diagrams.

ranges from 490 to 570 nm for **BAQ**, from 465 to 514 nm for **SFQ**, from 463 to 567 nm for **BLQ**, and from 479 to 570 nm for **XJQ**. One can see that the fluorescence colours change significantly in different solvents. **BLQ** is particularly sensitive to the polarity of the solvents. Its λ_{max}^{OPEF} is red-shifted by 104 nm, and the fluorescence changes from the blue region to the orange region. The Stokes shifts (Δv) exhibit the same solvent polarity dependencies as the λ_{max}^{OPEF} . These can be explained by the fact that the excited state may possess higher polarity than the ground state; the increased dipole–dipole interaction between the solute and solvent leads to a lowering of the energy level, which is accompanied by the positive solvatochromism.^[34]

The Lippert–Mataga equation can be used to estimate the dipole moment changes $(\mu_e - \mu_g)$ of the compounds with photoexcitation,^[35] as follows:

$$\Delta v = \frac{2\Delta f}{4\pi\varepsilon_0 hca^3} (\mu_{\rm e} - \mu_{\rm g})^2 + constant \tag{1}$$

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \tag{2}$$

in which $\Delta v = v_{abs} - v_{em}$ represents the Stokes shift, v_{abs} and v_{em} are the absorption and the emission frequency (cm⁻¹); *h* is Planck's constant, *c* is the velocity of light in vacuum, *a* is the Onsager radius, ε_0 is the permittivity of the vacuum, μ_e and μ_g are the dipole moments of the excited state and the ground state respectively; Δf is the orientation polarisability, ε is the



Fig. 4. Lippert–Mataga plots of the target compounds BAQ, SFQ, BLQ, and XJQ.

dielectric constant, and *n* is the refractive index. $(\mu_e - \mu_g)^2$ is proportional to the slope of the Lippert–Mataga plot.

From the plots of Δv versus Δf (Fig. 4), we find that the slopes of the fit line for the target compounds are 11590 (**BAQ**), 7141 (**SFQ**), 15111 (**BLQ**), and 9910 (**XJQ**) cm⁻¹ respectively. Considering the slopes and the Onsager radii together, the $\mu_e - \mu_g$ values may be arrange in the sequence **BAQ** > **BLQ** > **XJQ** > **SFQ**. The $\mu_e - \mu_g$ value is an important factor that affects the TPA properties. The values of Φ were determined using quinine sulfate in 0.5 mol L⁻¹ sulfuric acid as the standard ($\Phi = 0.546^{[33]}$). The value of Φ was obtained as follows:

$$\Phi_{\rm s} = \Phi_{\rm r} \frac{A_{\rm r}}{A_{\rm s}} \frac{n_{\rm s}^2 F_{\rm s}}{n_{\rm r}^2 F_{\rm r}} \tag{3}$$

where the subscripts s and r designate the sample and the reference respectively; A is the absorbance at the excitation wavelength, n is the refractive index of the relevant solution, and F is the integrated area under the corrected emission spectrum.

As shown in Table 1, with increasing solvent polarity, the Φ of **XJQ** varies slightly except in highly polar CH₃CN, whereas the Φ of **BAQ**, **SFQ**, and **BLQ** decreases monotonically and obviously. Considering the existence of an electron donor at one end and an electron acceptor at the other end, the latter response is likely due to the 'twisted intramolecular charge transfer' (TICT) effect.^[36] The three compounds **BAQ**, **SFQ**, and **BLQ** undergo strong ICT from the donor to the acceptor in the excited state, which is accompanied by a twist around the bond joining the donor and the acceptor. The Φ values of **XJQ** are significantly smaller than those of the other three compounds (**BAQ**, **SFQ**, and **BLQ**). As we know, the nitro group mostly acts as a fluorescence quencher owing to its non-radiative transfer, which consumes the excited energy by strong vibration of the group.^[37,38]

Two-Photon Properties

The non-linear optical properties of the target compounds **BAQ**, **SFQ**, **BLQ**, and **XJQ** are listed in Table 1. Representative twophoton excited fluorescence (TPEF) spectra of **BAQ** in THF are shown in Fig. 5.

As observed from Fig. 2, in the wavelength range 500–1000 nm, there is no linear absorption for the four target compounds. During the test, on excitation from 690 to 950 nm, laser-induced fluorescence appeared, which can be ascribed to frequency up-converted TPEF. The inset in Fig. 5b shows a log–log plot of the excited fluorescence signal versus the laser power; the slope value is 2.02 for **BAQ**. It provides direct evidence for the quadratic dependence of the excited fluorescence intensity on the input laser power, suggesting a two-photon excitation mechanism. The other compounds (**SFQ**, **BLQ**, and **XJQ**) also proved to have the same excitation mechanism.

It can be seen from Table 1 that the peak wavelengths of TPEF are clearly red-shifted by 27–67 nm compared with those of OPEF in THF and TOL, which was attributed to the fluorescence reabsorption effect within the solutions.^[39] The similarities between TPEF and OPEF indicate that both of the emissions for the given compounds are from the same excited state.

The σ values of the target compounds were measured using the two-photon induced fluorescence method. A femtosecond Ti : sapphire laser system (680–1080 nm, 80 MHz, 140 fs) was used as the light source. The incident average power of 500 mW was adjusted with a Glan prism. Then, the fluorescent emission was collected and recorded on an Ocean Optics USB 4000-FLG spectrofluorometer. The samples were dissolved in different solvents with a concentration of 1×10^{-3} mol L⁻¹. The σ values were determined with the following equation:

$$\sigma_{\rm s} = \frac{F_{\rm s}}{F_{\rm r}} \frac{\phi_{\rm r}}{\phi_{\rm s}} \frac{n_{\rm r}}{n_{\rm s}} \frac{c_{\rm r}}{c_{\rm s}} \sigma_{\rm r} \tag{4}$$

where the subscripts s and r denote the sample and the reference respectively; F and Φ represent the TPEF integral intensity and



Fig. 5. (a) Two-photon excited fluorescence spectra of **BAQ** in THF pumped by femtosecond laser pulses at 500 mW under different excitation wavelengths. (b) Two-photon excited fluorescence spectra of **BAQ** in THF at 830 nm under different input power levels. Inset is the logarithmic plot of the output fluorescence integral (I_{out}) of **BAQ** versus the input laser power (I_{in}).

the fluorescence quantum yield; *n* and *c* are the refractive index and the concentration of the solution. In the present work, we selected fluorescein in 0.1 mol L⁻¹ sodium hydroxide ($c = 1 \times 10^{-3} \text{ mol L}^{-1}$) as the reference; the σ value of the reference was taken from the literature.^[40]

The σ values of the target compounds in THF and TOL in the 690–950 nm region are displayed in Fig. 6. The experiments reveal that from 690 to 950 nm, the σ values are dependent on the excitation wavelength. The optimal excitation wavelengths in THF and TOL are both at 830 nm (**BAQ**, **BLQ**) and 770 nm (**SFQ**, **XJQ**). The maximum σ values in THF (TOL) were calculated to be 851 (545) GM for **BAQ**, 216 (83) GM for **SFQ**, 561 (309) GM for **BLQ**, and 447 (223) GM for **XJQ** respectively. All of the target compounds have larger a σ in THF than in TOL and follow the sequence **BAQ** > **BLQ** > **XJQ** > **SFQ** in both solvents.

In order to investigate the influence of different electron donors (or acceptors) on the σ of the target compounds, DFT calculations were performed using the *Gaussian 09* program and B3LYP 6-31G basis sets were used for the calculations. Their optimised structures are depicted in Fig. S1 (Supplementary Material). The energy levels and the electron cloud distributions of the frontier molecular orbitals are shown in Fig. 7. The HOMO and LUMO diagrams clearly show that the typical ICT processes have happened to all four target compounds. As for the three A- π -D compounds (**BAQ**, **SFQ**, and **BLQ**), most of



Fig. 6. Two-photon absorption cross-sections of the target compounds **BLQ**, **SFQ**, **BAQ**, and **XJQ** in (a) THF; and (b) TOL in the 690–950 nm regions.

the electron clouds of the HOMO are distributed on the triphenylamine (or thiophene, or pyrrole) donor and the styrene π -bridge, whereas in the LUMO, the electron cloud density localised on the donors decreases (especially for **BAQ**), and the electron cloud density on the terminal formyl acceptor increases significantly. For the A- π -A' compound (**XJQ**), the electron transfer is from the formyl group to the more strongly electronwithdrawing nitro group. The calculated HOMO–LUMO energy gaps (ΔE) are 2.64 (**BAQ**), 3.01 (**SFQ**), 2.83 (**BLQ**), and 2.85 (**XJQ**) eV respectively. The σ value shows a positive correlation with $\mu_e - \mu_g$, but negative correlation with ΔE . It is noted that the σ values follow the sequence **BAQ** > **BLQ** > **XJQ** > **SFQ**, which is consistent with the calculated results of ΔE and $\mu_e - \mu_g$.

Conclusions

In the present work, a series of all-*trans* A- π -D (A') compounds **BAQ**, **SFQ**, **BLQ**, and **XJQ** were easily synthesised using a three-step reaction route. Their linear absorption, one-photon excited fluorescence, two-photon absorption, and two-photon excited fluorescence were systematically investigated in various solvents. All the compounds show obvious solvatochromic effects and correspondingly large σ values. They may have a potential application as polarity-sensitive TPF probes.

Experimental

Materials and Methods

DMF and Et₃N were dried and distilled before use. All the other chemicals and solvents were purchased as reagent grade and used without further purification. Melting points were measured on an X-4 micromelting point apparatus without correction. ¹H NMR spectra were recorded using a Bruker Avance III 500 spectrometer in CDCl₃ or [D6]DMSO solvent with tetra-methylsilane (TMS) as an internal standard. FT-IR spectra were recorded on a Thermo Nicolet 6700 spectrometer using KBr pellets. Mass spectra were recorded on a Thermo LCQ TM Deca XP plus ion-trap mass spectrometer by electrospray ionization mass spectrometry (ESI-MS). Elemental analyses were determined with a Thermo Finnigan Flash EA 1112 apparatus.

The linear absorption spectra were recorded on a Shimadzu UV-2550 UV-visible spectrophotometer. The OPEF spectra were recorded using an RF-5301PC fluorescence spectrophotometer with the maximum absorption wavelengths as the excitation wavelengths. Φ was determined using quinine sulfate in 0.5 mol L⁻¹ sulfuric acid as the standard.

[(4-Ethenylphenyl)methyl]phosphonic Acid Diethyl Ester (**LSZ**)

LSZ was prepared via the method in reference [41]. Yield: 90.6 %.

4-[(1E)-2-(4-Ethenylphenyl)ethenyl]-N, N-diphenylbenzenamine (**3a**)

4-(Diphenylamino)benzaldehyde (15 mmol, 4.10 g), LSZ (10 mmol, 2.54 g), ^tBuOK (20 mmol, 2.24 g) and 7-mm stainless steel balls were placed in a grinding jar. The grinding jar was placed in a planetary ball-mill and stirred at 550 rotations per minute for 2 h at room temperature. The mixture became sticky and 60 mL CH₂Cl₂ was added to the jar, then the reaction mixture was washed twice with 200 mL water. The resulting organic layer was dried over MgSO4 and concentrated under vacuum. The residue was isolated by silica-gel column chromatography (light petroleum/ethyl acetate 10:1 v/v) to afford light-yellow needle crystals. Yield 2.99 g; 80.2 %, mp 192-193°C. δ_H ([D6]DMSO, 500 MHz) 7.55 (d, J 8.3, 2H), 7.52 (d, J 8.7, 2H), 7.47 (d, J 8.3, 2H), 7.33 (dd, J₁ 8.3, J₂ 7.6, 4H), 7.22 (d, J 16.4, 1H), 7.12 (d, J 16.4, 1H), 7.08 (t, J 7.4, 2H), 7.05 (dd, J₁) 8.5, J₂ 0.9, 4H), 6.96 (d, J 8.6, 2H), 6.73 (dd, J₁ 17.7, J₂ 11.0, 1H), 5.85 (d, J 17.9, 1H), 5.26 (d, J 11.3, 1H). v_{max} (KBr)/cm⁻¹ 3025, 1588, 1512, 1493, 1334, 1282, 1176, 970, 839, 753, 696, 533. m/z (ESI-MS) 374.4 [M + H]⁺. Anal Calc. for C₂₈H₂₃N: C 90.04, H 6.21, N 3.75; found C 90.16, H 6.23, N 3.79 %.

2-[(1E)-2-(4-Ethenylphenyl)ethenyl]thiophene (3b)

The synthesis of this compound was similar to **3a**. Off-white flaky crystals. Yield 76.6%, mp 129–131°C. $\delta_{\rm H}$ (CDCl₃, 500 MHz) 7.45 (d, *J* 8.4, 2H), 7.41 (d, *J* 8.4, 2H), 7.25 (d, *J* 16.1, 1H), 7.21 (d, *J* 5.1, 1H), 7.09 (d, *J* 3.4, 1H), 7.02 (dd, *J*₁ 5.1, *J*₂ 3.5, 1H), 6.93 (d, *J* 16.1, 1H), 6.73 (dd, *J*₁ 17.6, *J*₂ 10.9, 1H), 5.79 (dd, *J*₁ 17.5, *J*₂ 0.6, 1H), 5.27 (dd, *J*₁ 10.8, *J*₂ 0.6, 1H). $v_{\rm max}$ (KBr)/cm⁻¹ 3067, 1622, 1505, 1406, 1228, 1178, 960, 832, 691, 515. *m/z* (ESI-MS) 213.1 [M + H]⁺. Anal Calc. for C₁₄H₁₂S: C 79.20, H 5.70; found C 79.38, H 5.82%.

2-[(1E)-2-(4-Ethenylphenyl)ethenyl]-1-methyl-1H-pyrrole (3c)

The synthesis of this compound was similar to **3a.** Yellow crystalline powder. Yield 73.8%, mp 74–76°C. $\delta_{\rm H}$ (CDCl₃,

0 BAQ SFQ BLQ XJQ _1 30 ol LUMO + 1: -1.60 eV LUMO + 1: -2.45 eV -2LUMO: -2.21 eV Energy [eV] I UMO: -2 28 e\ LUMO: -2.39 eV -3LUMO: -3.06 eV - 4 HOMO: -5.04 eV -5 HOMO: -4.92 eV HOMO: -5.40 eV -6HOMO⁻ -5.91 eV HOMO - 1: -6.09 eV

Fig. 7. Energy levels and electron cloud distributions of the frontier molecular orbitals.

500 MHz) 7.43 (d, *J* 8.4, 2H), 7.39 (d, *J* 8.4, 2H), 6.98 (d, *J* 16.2, 1H), 6.86 (d, *J* 16.1, 1H), 6.72 (dd, J_1 17.6, J_2 10.9, 1H), 6.66 (t, *J* 2.0, 1H), 6.51 (dd, J_1 3.7, J_2 1.4, 1H), 6.17 (t, *J* 3.2, 1H), 5.76 (d, *J* 17.7, 1H), 5.24 (d, *J* 11.0, 1H). v_{max} (KBr)/cm⁻¹ 3026, 2941, 2816, 1698, 1667, 1624, 1598, 1470, 1425, 1300, 1060, 958, 821, 712. *m*/*z* (ESI-MS) 210.3 [M + H]⁺. Anal Calc. for C₁₅H₁₅N: C 86.08, H 7.22, N 6.69; found C 86.24, H 7.37, N 6.84 %.

1-Ethenyl-4-[(1E)-2-(4-nitrophenyl)ethenyl]benzene (3d)

The synthesis of this compound was similar to **3a.** Yellow crystalline powder. Yield 75.4%, mp 173–175°C. $\delta_{\rm H}$ ([D6] DMSO, 500 MHz) 8.25 (d, J 8.8, 2H), 7.88 (d, J 8.8, 2H), 7.68 (d, J 8.2, 2H), 7.55 (d, J 16.5, 1H), 7.53 (d, J 8.2, 2H), 7.45 (d, J 16.5, 1H), 6.77 (dd, J_1 17.7, J_2 11.1, 1H), 5.91 (d, J 17.7, 1H), 5.32 (d, J 11.1, 1H). $\nu_{\rm max}$ (KBr)/cm⁻¹ 3022, 1589, 1510, 1337, 1107, 974, 848, 516. *m/z* (ESI-MS) 252.2 [M + H]⁺. Anal Calc. for C₁₆H₁₃NO₂: C 76.48, H 5.21, N 5.57; found C 76.69, H 5.43, N 5.74 %.

4-[(1E)-2-[4-[(1E)-2-[4-(Diphenylamino)phenyl]ethenyl] phenyl]ethenyl]benzaldehyde (**BAQ**)

3a (1 mmol, 0.37 g), 4-bromobenzaldehyde (1 mmol, 0.18 g), Pd (OAc)₂ (0.03 mmol, 0.007 g), tri-*o*-tolylphosphine (0.13 mmol, 0.04 g), and anhydrous DMF/Et₃N were added to a three-necked flask equipped with a magnetic stirrer, a reflux condenser, and a nitrogen input tube. The mixture was stirred under N₂ at 120°C for 20 h. After cooling, the resulting mixture was poured into the ice water and filtered. The crude product was purified by silicagel column chromatography (light petroleum/ethyl acetate 12:1 v/v) to give an orange-yellow crystalline powder. Yield: 0.34 g, 71.3 %, mp 232–234°C. $\delta_{\rm H}$ ([D6]DMSO, 500 MHz) 9.98 (s, 1H), 7.91 (d, *J* 8.1, 2H), 7.83 (d, *J* 8.1, 2H), 7.66 (d, *J* 8.2, 2H), 7.53 (d, *J* 8.4, 2H), 7.50 (d, *J* 16.5, 1H), 7.39 (d, *J* 16.5, 1H), 7.08 (t, *J* 7.5, 2H), 7.05 (d, *J* 7.9, 4H), 6.96 (d, *J* 8.3, 2H). $\delta_{\rm C}$ ([D6]DMSO, 125 MHz) 192.32, 146.92,

146.87, 143.24, 138.47, 137.51, 136.72, 135.52, 134.98, 131.66, 130.02, 129.61, 128.37, 127.73, 127.37, 126.94, 126.69, 126.34, 124.22, 123.35, 122.89. $v_{\rm max}$ (KBr)/cm⁻¹ 3024, 1696, 1587, 1510, 1491, 1330, 1284, 1168, 965, 833, 752, 696, 546. *m/z* (ESI-MS) 478.1 [M + H]⁺. Anal Calc. for C₃₅H₂₇NO: C 88.02, H 5.70, N 2.93; found C 88.17, H 5.85, N 3.21 %.

2-[(1E)-2-[4-[(1E)-2-(4-Formylphenyl)ethenyl]phenyl] ethenyl]thiophene (**SFQ**)

The synthesis of this compound was similar to **BAQ**. Yellow crystalline powder. Yield 64.8 %, mp 220–222°C. $\delta_{\rm H}$ ([D6] DMSO, 500 MHz) 9.99 (s, 1H), 7.92 (d, *J* 8.3, 2H), 7.84 (d, *J* 8.3, 2H), 7.67 (d, *J* 8.4, 2H), 7.63 (d, *J* 8.4, 2H), 7.53 (d, *J* 16.2, 1H), 7.50 (d, *J* 16.4, 1H), 7.49 (d, *J* 5.1, 1H), 7.41 (d, *J* 16.4, 1H), 7.25 (d, *J* 3.4, 1H), 7.09 (dd, *J*_1 5.1, *J*_2 3.5, 1H), 6.98 (d, *J* 16.2, 1H). $\delta_{\rm C}$ ([D6]DMSO, 125 MHz) 192.33, 143.18, 142.32, 136.79, 135.80, 135.00, 131.56, 130.17, 130.01, 128.02, 127.91, 127.37, 127.18, 126.95, 126.71, 125.54, 122.33. $v_{\rm max}$ (KBr)/cm⁻¹ 3022, 1697, 1621, 1593, 1421, 1211, 1166, 958, 832, 706, 541. *m*/*z* (ESI-MS) 317.2 [M + H]⁺. Anal Calc. for C₂₁H₁₆OS: C 79.71, H 5.10; found C 79.94, H 5.28 %.

2-[(1E)-2-[4-[(1E)-2-(4-Formylphenyl)ethenyl]phenyl] ethenyl]-1-methyl-1H-pyrrole (**BLQ**)

The synthesis of this compound was similar to **BAQ**. Orangeyellow crystalline powder. Yield 56.7 %, mp 189–191°C. $\delta_{\rm H}$ ([D6]DMSO, 500 MHz) 9.99 (s, 1H), 7.92 (d, *J* 8.3, 2H), 7.84 (d, *J* 8.3, 2H), 7.64 (d, *J* 8.4, 2H), 7.60 (d, *J* 8.4, 2H), 7.50 (d, *J* 16.5, 1H), 7.38 (d, *J* 16.5, 1H), 7.24 (d, *J* 16.2, 1H), 6.90 (d, *J* 16.2, 1H), 6.81 (t, *J* 2.0, 1H), 6.51 (dd, *J*_1 3.7, *J*_2 1.6, 1H), 6.05 (t, *J* 3.1, 1H). $\delta_{\rm C}$ ([D6]DMSO, 125 MHz) 192.33, 143.32, 138.03, 134.90, 134.86, 131.76, 131.36, 130.01, 127.30, 126.87, 126.52, 126.23, 124.26, 123.96, 118.01, 108.06, 106.84, 33.69. $v_{\rm max}$ (KBr)/cm⁻¹ 3024, 2945, 2820, 1692, 1624, 1588, 1480, 1414, 1304, 1165, 1059, 957, 825, 716. *m/z* (ESI-MS) 314.3 [M + H]⁺. Anal Calc. for C₂₂H₁₉NO: C 84.31, H 6.11, N 4.47; found C 84.41, H 6.25, N 4.57%.



4-[(1E)-2-[4-[(1E)-2-(4-Nitrophenyl)ethenyl]phenyl] ethenyl]benzaldehyde (**XJQ**)

The synthesis of this compound was similar to **BAQ**. Yellow crystalline powder. Yield 68.1 %, mp 238–240°C. $\delta_{\rm H}$ ([D6] DMSO, 500 MHz) 10.00 (s, 1H), 8.26 (d, *J* 8.8, 2H), 7.93 (d, *J* 8.3, 2H), 7.89 (d, *J* 8.8, 2H), 7.85 (d, *J* 8.3, 2H), 7.74 (s, 4H), 7.58 (d, *J* 16.4, 1H), 7.53 (d, *J* 16.6, 1H), 7.49 (d, *J* 16.6, 1H), 7.45 (d, *J* 16.4, 1H). $\delta_{\rm C}$ ([D6]DMSO, 125 MHz) 192.38, 146.19, 144.00, 143.05, 136.90, 136.34, 135.11, 132.76, 131.42, 130.03, 127.79, 127.61, 127.43, 127.29, 127.05, 126.65, 124.05. $v_{\rm max}$ (KBr)/cm⁻¹ 3056, 1693, 1595, 1512, 1339, 1107, 964, 806, 541. *m/z* (ESI-MS) 356.4 [M + H]⁺. Anal Calc. for C₂₃H₁₇NO₃: C 77.73, H 4.82, N 3.94; found C 77.89, H 4.91, N 4.25 %.

Supplementary Material

Properties and spectra of target compounds **BAQ**, **SFQ**, **BLQ**, and **XJQ** are available in the Supplementary Material.

Acknowledgements

We are grateful for financial support from the Natural Science Foundation of Zhejiang province, China, (grant No. LY15B030006) and the National Natural Science Foundation of China (grant no. 21103151).

References

- M. Göppert-Mayer, Ann. Phys. 1931, 401, 273. doi:10.1002/ANDP. 19314010303
- [2] G. Zhang, Y. M. Sun, X. Q. He, W. J. Zhang, M. G. Tian, R. Q. Feng, R. Y. Zhang, X. C. Li, L. F. Guo, X. Q. Yu, S. L. Zhang, *Anal. Chem.* 2015, 87, 12088. doi:10.1021/ACS.ANALCHEM.5B02807
- [3] A. R. Atmeh, E. Z. Chong, G. Richard, A. Boyde, F. Festy, T. F. Watson, J. Microsc. 2015, 25, 7151.
- [4] N. Sheng, D. H. Liu, B. Gu, J. He, Y. P. Cui, *Dyes Pigm.* 2015, *122*, 346. doi:10.1016/J.DYEPIG.2015.07.011
- [5] S. Narayanan, A. Abbas, S. P. Raghunathan, K. Sreekumar, C. S. Kartha, R. Joseph, RSCAdv. 2015, 5, 8657. doi:10.1039/C4RA13024C
- [6] V. Vanyukov, G. M. Mikheev, T. N. Mogileva, A. P. Puzyr, V. S. Bondar, Y. P. Svirko, *Opt. Mater.* **2014**, *37*, 218. doi:10.1016/J.OPT MAT.2014.05.031
- [7] C. W. Christenson, A. Saini, B. Valle, J. Opt. Soc. Am. B 2014, 31, 637. doi:10.1364/JOSAB.31.000637
- [8] L. Li, Y. Q. Wu, Y. Wang, Chin. Opt. Lett. 2012, 10, 1.
- [9] D. Q. Hu, Y. L. Hu, W. H. Huang, Opt. Commun. 2012, 285, 4941. doi:10.1016/J.OPTCOM.2012.07.115
- [10] Q. L. Zou, H. Y. Zhao, Y. X. Zhao, Y. Y. Fang, D. F. Chen, J. Ren, J. Med. Chem. 2015, 58, 7949. doi:10.1021/ACS.JMEDCHEM. 5B00731
- [11] E. Secret, M. Maynadier, A. Gallud, A. Chaix, E. Bouffard, M. Gary-Bobo, N. Marcotte, O. Mongin, K. E. Cheikh, V. Hugues, M. Auffan, C. Frochot, A. Morère, P. Maillard, M. Blanchard-Desce, M. J. Sailor, M. Garcia, J. O. Durand, F. Cunin, *Adv. Mater.* 2014, *26*, 7643. doi:10.1002/ADMA.201403415
- [12] B. Hamed, T. Haimberger, V. Kozich, A. Wiehe, K. Heyne, *Photo-chem. Photobiol.* 2014, 295, 53. doi:10.1016/J.JPHOTOCHEM.2014. 09.006
- [13] L. V. Chinta, L. Lindvere, A. Dorr, B. Sahota, J. G. Sled, B. Stefanovic, *NeuroImage* **2012**, *61*, 517. doi:10.1016/J.NEUROIMAGE.2012.04. 009
- [14] E. E. Cho, J. Drazic, M. Ganguly, B. Stefanovic, K. Hynynen, J. Cereb. Blood Flow Metab. 2011, 31, 1852. doi:10.1038/JCBFM.2011.59
- [15] W. Tao, M. H. Soonpaa, L. J. Field, P. S. Chen, A. B. Firulli, W. N. Shou, M. Rubart, *Pediatr. Cardiol.* **2012**, *33*, 929. doi:10.1007/S00246-012-0314-8

- [16] Z. J. Hu, J. X. Yang, Y. P. Tian, H. P. Zhou, X. T. Tao, G. B. Xu, W. T. Yu, X. Q. Yu, M. H. Jiang, *J. Mol. Struct.* 2007, 839, 50. doi:10.1016/ J.MOLSTRUC.2006.10.044
- [17] Y. Zhao, A. M. Ren, J. K. Feng, X. Zhou, X. C. Ai, W. J. Su, *Phys. Chem. Chem. Phys.* **2009**, *11*, 11538. doi:10.1039/B908415K
- [18] R. Nazir, F. Bourquard, E. Balčiūnas, S. Smoleń, D. Gray, N. V. Tkachenko, M. Farsari, D. T. Gryko, *ChemPhysChem* 2015, *16*, 682. doi:10.1002/CPHC.201402646
- [19] H. R. Li, L. Yang, J. Liu, C. F. Wang, F. Gao, S. T. Zhang, J. Fluoresc. 2011, 21, 393. doi:10.1007/S10895-010-0728-8
- [20] S. P. Anthony, S. Varughese, S. M. Draper, J. Phys. Org. Chem. 2010, 23, 1074. doi:10.1002/POC.1757
- [21] J. M. Hales, J. Matichak, S. Barlow, S. Ohira, K. Yesudas, J.-L. Bredas, J. W. Perry, S. R. Marder, *Science* 2010, *327*, 1485. doi:10.1126/SCI ENCE.1185117
- [22] Y. P. Tian, L. Li, J. Z. Zhang, J. X. Yang, H. P. Zhou, J. Y. Yu, P. P. Sun, L. M. Tao, Y. H. Guo, C. K. Wang, H. Xing, W. H. Hung, X. T. Tao, M. H. Jiang, *J. Mater. Chem.* **2007**, *17*, 3646. doi:10.1039/B703853D
- [23] Q. Q. Li, C. Zhong, J. Huang, Z. L. Huang, Z. G. Pei, J. Liu, J. G. Qin, Z. Li, J. Phys. Chem. B 2011, 115, 8679. doi:10.1021/JP2015484
- [24] Q. Zhang, J. S. Luo, L. L. Ye, H. Huang, B. Huang, J. Zhang, J. Y. Wu, S. Y. Zhang, Y. P. Tian, *J. Mol. Struct.* **2014**, *1074*, 33. doi:10.1016/ J.MOLSTRUC.2014.04.058
- [25] F. Jin, Z. B. Cai, J. Q. Huang, S. L. Li, Y. P. Tian, J. Mol. Struct. 2015, 1093, 33. doi:10.1016/J.MOLSTRUC.2015.03.036
- [26] Z. B. Cai, L. F. Liu, C. Kong, Y. X. Zhu, Acta Phys. Chim. Sin. 2014, 30, 164.
- [27] A. Schulz, H. Meier, *Tetrahedron* 2007, 63, 11429. doi:10.1016/J.TET. 2007.08.064
- [28] N. Armaroli, F. Barigelletti, P. Ceroni, J. F. Ckert, J. F. Nierengarten, Int. J. Photoenergy 2001, 3, 33. doi:10.1155/S1110662X01000046
- [29] J. Kumpf, U. H. F. Bunz, Chem. Eur. J. 2012, 18, 8921. doi:10.1002/ CHEM.201200930
- [30] M. Jørgensen, F. C. Krebs, J. Org. Chem. 2005, 70, 6004. doi:10.1021/ JO0506783
- [31] J. McNulty, D. McLeod, *Tetrahedron Lett.* 2011, 52, 5467. doi:10.1016/ J.TETLET.2011.08.040
- [32] G. G. Dubinina, R. S. Price, K. A. Abboud, G. Wicks, P. Wnuk, Y. Stepanenko, M. Drobizhev, A. Rebane, K. S. Schanze, J. Am. Chem. Soc. 2012, 134, 19346. doi:10.1021/JA309393C
- [33] G. A. Crosby, J. N. Demas, J. Phys. Chem. 1971, 75, 991. doi:10.1021/ J100678A001
- [34] W. Li, M. D. Yang, L. P. Wang, W. J. Zhu, L. N. Ye, J. Y. Wu, Y. P. Tian, H. P. Zhou, *Dyes Pigm.* 2014, 107, 133. doi:10.1016/J.DYEPIG. 2014.03.034
- [35] J. R. Lakowicz, *Principles of Fluorescence Spectroscopy* (3rd edn) 2006 (Springer: New York, NY).
- [36] W. B. Wu, C. Liu, M. L. Wang, W. Huang, S. R. Zhou, W. Jiang, Y. M. Sun, Y. P. Cui, C. X. Xu, *J. Solid State Chem.* **2009**, *182*, 862. doi:10. 1016/JJSSC.2008.12.003
- [37] M. Dai, W. P. Zhu, Y. F. Xu, X. H. Qian, Y. Liu, Y. Xiao, Y. You, J. Fluoresc. 2008, 18, 591. doi:10.1007/S10895-007-0303-0
- [38] J. Santos-Pérez, C. E. Crespo-Hernández, C. Reichardt, C. R. Cabrera, I. Feliciano-Ramos, L. Arroyo-Ramírez, M. A. Meador, *J. Phys. Chem. A* 2011, *115*, 4157. doi:10.1021/JP111174P
- [39] H. P. Zhou, Z. Zheng, G. Y. Xu, Z. P. Yu, X. F. Yang, L. H. Cheng, X. H. Tian, L. Kong, J. Y. Wu, Y. P. Tian, *Dyes Pigm.* 2012, *94*, 570. doi:10.1016/J.DYEPIG.2012.03.017
- [40] C. Xu, W. W. Webb, J. Opt. Soc. Am. B 1996, 13, 481. doi:10.1364/ JOSAB.13.000481
- [41] J. X. Yang, X. T. Tao, C. X. Yuan, Y. X. Yan, J. Am. Chem. Soc. 2005, 127, 3278. doi:10.1021/JA043510S