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Solvent dependent linear and nonlinear optical properties of triphenylamine unit incorporated difluoroboron β -diketonate complexes

Chenggong Ju^{a,c,1}, Yongzhu Zhou^{a,b,1}, Sergey Semin^c, Guang Yang^a, Paul Tinnemans^c, Yulong Duan^c, Yaqing Feng^{a,e,*}, Theo Rasing^c, Jialiang Xu^{a,d,**}

^a School of Chemical Engineering and Technology, Tianjin University, Yaguan Road 135, Tianjin, 300350, PR China

^b School of Science, Tianjin Chengjian University, Tianjin, 300384, PR China

^c Radboud University, Institute for Molecules and Materials (IMM), Heyendaalseweg 135, 6525AJ, Nijmegen, the Netherlands

^d School of Materials Science and Engineering, Nankai University, Tongyan Road 38, Tianjin, 300350, PR China

^e Collaborative Innovation Center of Chemical Science and Engineering, Tianjin University, Weijin Road 92, Tianjin, 300072, PR China

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ABSTRACT

In this work, four intramolecular charge transfer (ICT) compounds, **TBT**, **TVBVT**, **TSBST** and **TSVBVST**, with difluoroboron β -diketonate as the electron acceptor, triphenylamine unit as the electron donor and different π -conjugated bridges have been synthesized. The linear absorption and emission spectra in different organic solvents indicate a positive solvato-chromism. The multilinear regression analyses of the linear optical spectra in different solvents indicate that the solvato-chromism is mainly caused by the polarity/dipolarity properties of the solvents and possibly the halogen-halide interaction. Time-dependent density functional theory (TD-DFT) calculations were used to investigate the charge density difference between the ground and excited states of the complex molecules of interest and the ICT processes of the excited molecules were verified. The nonlinear optical properties of the molecules were studied using a Z-scan technique. It is found that not only the structure of the molecules influences the nonlinear optical properties, but that also the solvent-solute interaction plays an important role.

1. Introduction

Organic luminescent materials have gained extensive attention in recent decades for their wide applications in organic light emitting diodes (OLEDs) [1,2], mechano-chromic materials [3–5], chemical or biological sensing and imaging [6–10]. Among these, the organoboron luminogens [11–13] are particularly promising for their desirable photophysical and electronic properties, such as high carrier mobility, high molar absorption coefficients and high fluorescence quantum yields [14–16]. Their diverse reactivity profiles and high tolerance for structure modification create a great potential for applications of these molecules [17–19]. In particular, difluoroboron β -diketonates (BF₂bdks), which are a kind of tetra-coordinate organoboron dye easily obtained through Claisen condensation and modified by the different substitutions at the 4, 6-positions [20], have gained considerable attention for their stability and versatile photophysical properties [7,12,21]. Fraser [22] et al. reported the recoverable mechano-chromic

luminescence (ML) of the cyan polymorph of the difluoroboron avobenzene, which was confirmed to be facilitated by the slip plane [23] in the structure. Later, through the modification of the aromatic rings, some other BF₂bdks compounds with ML property were synthesized [11,24]. It turned out that the substitutions at 4, 6-positions of BF₂bdks influence the packing modes of the molecules and the external pressure induces the rearrangement of the molecules and thus their ML properties [11,24]. Lu [25] et al. found that the length of the π spacer influences the self-assembly behavior of the BF₂bdks by affecting the intermolecular π - π interactions. Not only the structure of the BF₂bdks molecule itself is significant, but also the medium in which the molecule exist will play an important role for the properties of the BF₂bdks molecule. For example, the restrictions of the bond rotation of the molecules in a rigid environment will cause aggregation induced emission enhancement (AIEE) [13] and the hindrance of the intramolecular motion of the molecules in such environment will offer phosphorescence due to the suppression of relaxations of the triplet

* Corresponding author. School of Chemical Engineering and Technology, Tianjin University, Yaguan Road 135, Tianjin, 300350, PR China.

** Corresponding author. School of Chemical Engineering and Technology, Tianjin University, Yaguan Road 135, Tianjin, 300350, PR China.

E-mail addresses: yqfeng@tju.edu.cn (Y. Feng), jialiang.xu@nankai.edu.cn (J. Xu).

¹ These two authors contributed equally to this work.

Scheme 1. Synthetic routes for the four diboronfluoron β -diketonates.

manifold [26]. Fraser [27] et al. have synthesized a series of aromatic difluoroboron β -diketonate complexes and found that both the π conjugation and the media had remarkable effects on the photophysical properties of the compounds. Later they successfully modulated the emissive properties and realized the effective oxygen sensing of the difluoroboron naphthyl-phenyl β -diketonate polylactide materials through the introduction of the heavy atom, tuning the dye attachment site and adjusting the polymer molecular weight [28]. Therefore, it is necessary to take the media and the corresponding interactions into account when considering the molecular design and applications of BF_2 bdkes [21,29,30].

With the emergence of modern technologies, like optical telecommunications, organic nonlinear optical (NLO) materials have attracted much attention for their merits of high response speed, chemical tunability and variable synthetic strategies [31–34]. Organic ICT compounds are ideal candidates as third-order nonlinear optical materials because of their inherent high hyperpolarizabilities [35–37]. Among these molecules, the quadrupolar D- π -A- π -D structure is highlighted for its excellent nonlinear optical properties [38–41], with large two-photon absorption (TPA) cross-sections [42,43]. The intramolecular charge transfer, which occurs in systems containing both donor and acceptor parts, will influence the TPA properties strongly [44,45]. Different strategies like modifications of donor or acceptor moieties and the adjustment of the conjugation length have been attempted to increase the TPA cross sections [43,46–49]. The ICT and the charge distributions also have a significant effect on the nonlinear optical properties of the molecules [50]. The D-A conjugation and the linkage spacer will influence the distributions of the molecular orbitals and the energy gap [51] of the concerned molecules. The strong π -electron delocalization [52] which is beneficial for the charge transfer and the extension of the conjugation length [53] can both increase the nonlinear optical properties. Similar to the situation for the TPA, azobenzene [54,55], thiophene [56,57] and styryl units [53,58] etc. have been adopted to examine the influence of D/A and the conjugation bridge on the nonlinear optical properties in different molecular systems.

It is well known that the triphenylamine moiety has strong electron-donating ability, which can be enhanced in conjugated systems [59,60].

As a heterocyclic ring, the thiophene unit has reduced aromaticity and higher electron density, which is suitable for the application in NLO chromophores as the conjugation bridge [57,61]. In this study, through the introduction of triphenylamine moiety and thiophene ring unit into the BF_2 bdkes conjugated system and tuning the conjugation extension with the vinyl moiety, we synthesized four ICT compounds, namely, **TBT**, **TVBVT**, **TSBST** and **TSVBVST**, and studied their optical properties under various conditions. The solvato-chromism of the four compounds was investigated and multiple linear regression revealed that solute-solvent interaction was significant for the linear optical behavior of the four compounds. Theoretical calculations verified the ICT process during the excitation process of the compounds. The Z-scan measurement was used to explore the effect of the solvent-solute interaction on the nonlinear optical properties of the four compounds. We found that a high third-order NLO response could be reached through the combination of the adjustment of the molecular structure and the usage of solvent-solute interaction, which will help the rational design of organic linear and nonlinear optical materials in the future.

2. Results and discussion

2.1. Synthesis

The synthetic route to the desired compounds 4, 4'-((2, 2-difluoro-2H-1 λ^3 , 3, 2 λ^4 -dioxaborinine-4, 6-diyl) bis (N,N-diphenylaniline) (**TBT**), 4, 4'-((2, 2-difluoro-2H-1 λ^3 , 3, 2 λ^4 -dioxaborinine-4, 6-diyl) bis (thiophene-5, 2-diyl)) bis(N, N-diphenylaniline) (**TSBST**), 4, 4'-((1E, 1'E)-(2, 2-difluoro-2H-1 λ^3 , 3, 2 λ^4 -dioxaborinine-4, 6-diyl) bis(ethene-2, 1-diyl)) bis(N, N-diphenylaniline) (**TVBVT**) and 4, 4'-((1E, 1'E)-(2, 2-difluoro-2H-1 λ^3 , 3, 2 λ^4 -dioxaborinine-4, 6-diyl) bis(ethene-2, 1-diyl)) bis(thiophene-5, 2-diyl)) bis(N, N-diphenylaniline) (**TSVBVST**) is shown in Scheme 1. For simplicity, we use different letters (**T** for the triphenylamine unit, **B** for the difluoroboron core, **S** for the thiophene ring and **V** for the vinylene linkage) to represent different units to get the abbreviations for the four compounds.

Compound **TBT** was synthesized as a magenta powder via the condensation of methyl 4-(diphenylamino) benzoate (**1**) and 1-(4-(diphenylamino) phenyl) ethan-1-one (**2**) followed by the complexation

with boron trifluoride diethyl etherate ($\text{BF}_3\cdot\text{Et}_2\text{O}$) in a 53% yield. Compound **TSBST** was synthesized following the same route except that the start materials **1** and **2** were replaced by methyl 5-(4-(diphenylamino) phenyl) thiophene-2-carboxylate (**3**) and 1-(5-(4-(diphenylamino) phenyl) thiophen-2-yl) ethan-1-one (**4**), respectively. After isolation, the **TSBST** was obtained as a dark purple powder in a 31% yield. The aldol condensation of 4-(diphenylamino) benzaldehyde with difluoroboron acetylacetone complex (**6**) gave compound **TVBVT** as an amaranth solid in a 34% yield. The similar condensation of 5-(4-(diphenylamino) phenyl) thiophene-2-carbaldehyde (**5**) and **6** gave compound **TSVBVST** as a purple black powder in a 28% yield. Compound **3** was synthesized through the Suzuki coupling of (4-(diphenylamino) phenyl) boronic acid and methyl 5-bromothiophene-2-carboxylate, and a greenish yellow powder was obtained with a yield of 58%.

The chemical structures of the new compounds were confirmed using ^1H NMR, ^{13}C NMR spectroscopy and high resolution mass spectrometer (HRMS) (Fig. S1–Fig. S15, SI). The details of the synthesis route could be found in the experimental section below.

2.2. Crystal structures of **TSBST** and **TSVBVST**

Single crystals of **TSBST** (Table S1) were obtained by the solvent exchange method. In a typical procedure, 20 mg of **TSBST** was dissolved in 2 mL of CHCl_3 in a vial, and then 6 mL of MeOH was added slowly to form a new layer on the surface of the solution. After the diffusion, dark purple parallelepiped-like crystals were obtained, and the single crystal X-ray diffraction (XRD) analysis suggest that the compound crystallizes with a space group of $\text{P}\bar{1}$ and unit cell dimensions of $a = 10.244(6)$ Å, $b = 14.438(8)$ Å, $c = 15.418(8)$ Å, $\alpha = 99.230(16)^\circ$, $\beta = 92.44(2)^\circ$, $\gamma = 104.17(3)^\circ$ (CCDC number: 1859839). For **TSVBVST**, purple black crystals (Table S2) were obtained by an antisolvent method with CHCl_3 and acetone as good and poor solvent ($v/v = 1:1$), respectively. The unit cell of **TSVBVST** is triclinic with a space group of $\text{P}\bar{1}$ and unit cell parameters of $a = 9.7172(4)$ Å, $b = 14.2279(6)$ Å, $c = 17.1777(7)$ Å, $\alpha = 74.6883(14)^\circ$, $\beta = 79.2208(13)^\circ$, $\gamma = 86.5859(14)^\circ$ (CCDC number: 1859840). We failed to obtain crystals of **TBT** and **TVBVT** although different methods like slow evaporation, solvent exchange and vapor diffusion have been attempted.

In the unit cell of the **TSBST** crystal, the two molecules are arranged in an antiparallel way, with the $\text{C}\cdots\text{H}\cdots\pi$ interactions and $\pi\cdots\pi$ interactions between the phenyls of triphenylamine units, $\text{C}\cdots\text{S}\cdots\pi$ interactions between thiophene units and triphenylamine units and $\text{F}\cdots\pi$ interactions between F atom and the thiophene units (Fig. 1a) as the driving forces. Along the crystallographic c -axis, the molecules are connected to form a molecular chain through the $\text{O}\cdots\text{H}$ and $\text{B}\cdots\text{H}$ interactions (Fig. 1b). With the aforementioned interactions between the molecules in the unit cell, the chains are arranged in a centrosymmetric way to form the crystal. However, the CHCl_3 molecules are embedded in the structure of the crystal of **TSVBVST** (Fig. 1c). It is clear that the interactions of the $\text{C}\cdots\text{Cl}\cdots\text{H}$ and $\text{B}\cdots\text{F}\cdots\text{H}$, together with the $\pi\cdots\pi$ interactions, make the two molecules and the CHCl_3 to form a “sandwich” structure in the unit cell. The CHCl_3 molecule is significant for the formation of the molecular chain along the a -axis, through the $\text{C}\cdots\text{Cl}\cdots\text{H}$, $\text{B}\cdots\text{F}\cdots\text{H}$ and $\text{B}\cdots\text{H}$ interactions the molecules are linked together (Fig. 1d). The chains are then packed in an antiparallel way to form a centrosymmetric configuration. We can also see that in the unit cell, for **TSBST**, the two molecules slide away from each other mainly along the molecular long-axis, while for **TSVBVST** the deviation direction is in the molecular short-axis direction. It is probably related with both the stereo hindrance and the interaction between the CHCl_3 and the molecule (for **TSVBVST**).

2.3. Photophysical properties

The linear optical properties of the four compounds (**TBT**, **TVBVT**,

TSVBVST and **TSBST**) were investigated by measuring their UV–Vis absorption and emission spectra in different solvents (concentration: $\sim 10^{-6}$ M). As depicted in Fig. S16, the wavelengths of the absorption spectra for the four compounds lie in the range of 522–721 nm. The absorption bands can be assigned to the ICT transition, which could be deduced from the solvent-dependent fluorescence emission spectral changes [62]. For the same compound, one can see that the maximum absorption peak shows a red shift with the increase of the solvent polarities (hexane < toluene < tetrahydrofuran (THF) < chloroform (CHCl_3) < *N,N*-dimethyl formamide (DMF)), demonstrating a weak positive solvato-chromism [63]. This indicates that the compounds have small dipole moments and the polar environments cause small differences in dipole moments of the ground state of the same compound [64]. For different compounds in the same solvent, with the conjugation length being longer, the wavelength of the maximum absorption peak becomes longer. For example, **TBT** shows an absorption peak at 483 nm while **TVBVT** shows one at 556 nm. This is consistent with the general fact that the increased conjugation leads to red-shifted emission [65]. As shown in Fig. 2, the emission spectra for the same compound shows a bathochromic shift from the nonpolar solvent hexane to the high polar solvent DMF (for **TSBST** or **TSVBVST**, the emission in DMF is too weak to be detectable). This may be ascribed to the stabilization of the excited state in polar solvents, that is, the dipole moment of the excited state is larger than that of the ground state. The stabilized molecular excited state in a polar environment possesses lower energy levels and emits at a longer wavelength [66,67]. The comparison of the emission spectra for the different compounds in the same solvent shows the same trend, that the increased conjugation induces a red-shift of the emission. Although it is not obvious in the absorption, it is clear that the emission spectrum becomes wider from hexane to DMF with the enhancement of the solvent polarity. These phenomena are ascribed to the ICT transition process from the triphenylamine (TPA) group to the difluoroboron (BF_2) part, along with a solvent relaxed emissive state [68–70].

Stokes shifts, which are the differences between the wavelengths of emission and absorption maxima, indicate the amount of consumed energy in the nonradiative process [71] and the geometry change from the ground state to the excited state [28]. As illustrated in Table S3, with increasing polarity of the solvent, the Stokes shift becomes larger for the same compound. When the conjugation length becomes longer, the Stokes shift becomes bigger too. For **TSVBVST** in THF, the Stokes shift reaches > 95 nm. These facts reveal the strong ICT and conformation relaxation processes in the excited state [28,66]. For the molecules with ICT, the dipole moment of the molecule in the excited state will interact with the dipole moment of the solvent, especially in high polar solvents. This kind of interaction will reduce the energy level of the excited state and enhance the rate of nonradiative decay [66]. With extended conjugation, the motion freedom of the molecules may increase and the molecules will have stronger geometry relaxation in the excited state and more energy loss through nonradiative decay [72]. The ICT process can also decrease the emission intensity [73], which can explain the almost undetectable emission from the four compounds in their DMF solutions. The fluorescence decay profiles of the four compounds can be well fitted by applying a double-exponential function, with fluorescence lifetimes in the nanosecond time scale. The fluorescence lifetime is related to the conformational stability of the excited molecule [66]. From hexane to DMF, with increasing polarity of the solvent, the fluorescence lifetime generally shows a rising trend. This is in accordance with the fact that the excited state of the ICT molecule is polar and can be stabilized in a polar solvent. The fluorescence lifetime of the molecules in different solvents may also be influenced by the viscosity and some other solvent-solute interactions [66], so there are fluctuations of the fluorescence lifetime. In toluene, the relative quantum yields (Φ) are 0.90, 0.76, 0.78 and 0.52 for **TBT**, **TVBVT**, **TSBST** and **TSVBVST**, respectively, showing that they are strongly emissive in non-polar solvents, which is characteristic for ICT

Fig. 1. The packing mode of the **TSBST** and **TSVBVST** crystals. a) packed molecules of **TSBST** in a unit cell, viewed along the *b*-axis; b) the molecular chain of **TSBST** along the *c*-axis, viewed along the *a*-axis. c) packed molecules of **TSVBVST** in a unit cell, viewed along the *a*-axis; d) the molecular chain of **TSVBVST** along the *a*-axis, viewed along the *c*-axis.

molecules [74]. The decay process is mainly radiative in non-polar solvents, while in polar solvents the stabilization of charge separation decreases the radiative decay process [59,66,74].

Among the five solvents, CHCl_3 is special. Although the polarity of CHCl_3 is smaller than that of DMF, the wavelength of the absorption and the emission band of their solutions in CHCl_3 for the four compounds are almost the same or larger than that of their solutions in DMF. The interactions of the fluorine in the BF_2 units of the four compounds and the chlorine in CHCl_3 ($\text{B-F}\cdots\text{Cl-C}$) may cause the destabilization of the ground state and raise its energy level. This kind of halogen-halide interaction will narrow the energy gap between the ground and excited state, and thus it brings about the bathochromic shift of the absorption spectra [30,75–77].

2.4. Solvato-chromism

The solute-solvent interactions can be divided into specific and nonspecific ones: the former to be donor-acceptor or base-acid like interactions, and the latter to be dipole-dipole interactions [78]. In order to evaluate the influences on absorption and fluorescence, these interactions have been parameterized: π^* for solvent polarity/dipolarizability, α for the H-bond donor (HBD) ability, β for the H-bond acceptor (HBA) ability [79]. Gu [80] et al. have established a mathematical model to scale these parameters in a scale of 0–1. To get a clear insight into the influence of the different solvation modes on the absorption and fluorescence, the multiple linear regression [79] analysis method was used according to equation (1):

$$y = y_0 + a\alpha + b\beta + c\pi^* \quad (1)$$

where y_0 denotes the spectroscopic property under consideration in the gas phase and a , b and c are the corresponding regression coefficients.

The physicochemical properties analyzed here are the absorption maxima ν_{abs} (in cm^{-1}) and the emission maxima ν_{em} (in cm^{-1}). The values of α , β and π^* used in the analysis for the concerned solvents are directly taken from the literature [80]. The regression results for the four compounds of interest are listed in Table 1. It can be seen from the values of R^2 , which is the criterion for goodness-of-fit, that the set $\langle\alpha, \beta, \pi^*\rangle$ shows medium to good fits (0.97, 0.89, 0.90 and 0.70) to ν_{abs} of the four compounds. Medium fits (0.88, 0.92, 0.85 and 0.79) are also

obtained for the multilinear regression analysis for ν_{em} of the four compounds (for **TSBST** and **TSVBVST**, the regressions are done using two parameters, and the R^2 listed in the table are the biggest among the three two-parameter-regressions for each compound, respectively). The effect that we didn't take into account in the regression analysis was the aforementioned halogen-halide interaction. Thus it might be that the halogen-halide interaction had significant effects on the ground states of the molecules. It can be deduced from the decreasing R^2 that the halogen-halide interaction maybe play an important role when the conjugation of the D- π -A- π -D compound becomes longer.

The three parameters α , β and π^* are mutually independent, which allows us to separate the contribution of polarity/dipolarity, HBD and HBA to the solute-solvent interactions. The regression analysis of ν_{abs} and ν_{em} with only one variable π^* was done with the results shown in Fig. 3. Compared with the results for ν_{abs} from Table 1, we found that the R^2 for regression analysis with three variables were close to the results with only π^* , meaning that it was the polarity/dipolarity of the solvents which mainly influenced the UV-Vis absorption. With respect to ν_{em} , the polarity/dipolarity of the solvents plays an important role as can be seen from the R^2 values (with exception of **TSVBVST**) in Fig. 3b. For **TSVBVST**, the one-variable-regression analysis showed the HBA ability of the solvent played an important role in the solvent-solute interactions, which can be deduced from the R^2 value (Fig. S18-Fig. S21, SI).

For ν_{abs} and ν_{em} , with the conjugation length becoming longer, the value of R^2 for the regression analysis with three parameters or only one parameter gets smaller. It may tell us that the halogen-halide interaction tends to have a stronger influence on the larger conjugation system for the difluoroboron β -diketonate complexes [30].

2.5. Theoretical calculations

The ground state calculations of the isolated dye **TBT**, **TVBVT**, **TSBST** and **TSVBVST** have been performed with density functional theory (DFT) while TD-DFT calculations have been used to determine the vertical excitation states of the compounds. All the calculations were carried out at B3LYP/6-311g* level using the Gaussian 09 code [81]. The charge density differences between the ground and excited states of the four compounds have been calculated by using the

Fig. 2. Photopictures (excited at 365 nm using a UV lamp) and fluorescence spectra of four compounds (10^{-6} M) in five solvents (hexane, toluene, THF, CHCl_3 , DMF). a) TBT, b) TVBVT, c) TSBST and d) TSVBVST. For TSBST and TSVBVST, the emission is too weak to be detectable in DMF.

Table 1

Multiple linear regression coefficients^a for TBT, TVBVT, TSBST and TSVBVST.

Compound	a	b	c	y_0	R^2
TBT	−2651	−66	−1156	20678	0.97
TVBVT	−3041	25	−1134	17977	0.89
TSBST	−3334	−563	−933	18384	0.90
TSVBVST	−3081	−109	−757	16827	0.70
TBT	−5245	−297	−1795	19016	0.88
TVBVT	−7591	−750	−1461	17039	0.93
TSBST ^a	−4202	−	−2437	17311	0.85
TSVBVST ^a	1988	−3188	−	15689	0.79

^a For TSBST and TSVBVST, the regression analysis was fitted with two variables, the listed value here are the set with biggest R^2 within the three sets.

Multiwfn program [82]. From Fig. 4, we could see that the LUMOs of the four compounds were mainly localized in the central difluoroboron β -diketonate while the HOMOs mainly localized in the triphenylamine units. The charge density difference diagrams show that the electron density decreases in the triphenylamine units while it increases in the central difluoroboron β -diketonate units when the molecules of the four compounds get excited (The blue and green colours mean that the

electron density decreases and increases in the areas, respectively, accompanying the electronic excitation, as shown in Fig. 4). This indicates that the ICT process happened in the excited molecules, which corroborates with the linear spectra. On the other hand, the calculated energy levels and the energy gaps (Fig. S17) confirm the observation of a red-shift in the linear spectra as the conjugation length of the molecules becomes longer.

2.6. Nonlinear optical properties

For the linear optical properties of the four compounds, the solvent-solute interaction has a significant effect on the solvato-chromism among which, the halogen-halide interaction seems to be extraordinary. In order to study the effect of halogen-halide interaction on the nonlinear optical properties of the four compounds of interest, we have made third-order nonlinear refractive measurements. CHCl_3 and THF were chosen as the solvents for their similar polarities to minimize the effect of the dipole-dipole interaction on the nonlinear behavior.

The third-order nonlinear refractive index n_2 of the four fluorophores were calculated in CHCl_3 and THF at a concentration of 1×10^{-5} M. The closed-aperture (CA) Z-scan measurement technique

Fig. 3. Correlation of a) absorbance and b) fluorescence maxima (in cm^{-1}) of the four compounds in five solvents with the polarity/dipolarity of the solvents.

Fig. 4. Molecular orbital surfaces in the optimized ground-state structures and the charge density differences from the ground state to the excited state of a) TBT, b) TVBVT, c) TSBST and d) TSVBVST. For the LUMO and HOMO orbital diagrams, the white, grey, yellow, red, pink, light blue balls correspond to hydrogen, carbon, sulfur, oxygen, boron and fluorine atoms, respectively. For the charge density differences, the blue and green areas signify decrease and increase in electron density accompanying the electronic excitation, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Fig. 5. CA z-scan curves of normalized transmittance of the four compounds in CHCl_3 and THF, respectively, with the concentration of the solutions being 10^{-4} M and the laser wavelength being 800 nm a) in CHCl_3 , laser power: 60 mW and b) in THF, laser power: 70 mW.

was employed using a home-built setup with a femtosecond laser pulse (pulse width 100 fs) as the light source with a wavelength of 800 nm. In this method, thin-layer samples of the four compounds in CHCl_3 or THF held in a 1 mm-thick quartz cuvette were moved along the beam direction and the transmitted radiation through an aperture (on axis) was recorded. Because of its good nonlinear optical response, CS_2 was chosen as a reference to calibrate the system [83].

The normalized CA Z-scan curves of the four compounds (TBT, TVBVT, TSBST and TSVBVST) in CHCl_3 and THF are shown in Fig. 5. The curves show the dependence of the transmittance on the sample position relative to the focal point of the lens ($z = 0$). The normalization of data here was over the transmission intensity at the position $z = 0$. The peak-valley configuration indicates the prominent self-defocusing effect of light in the four studied fluorophores [84]. In the CA Z-scan measurements, usually there will be an influence of nonlinear absorption [85,86]. The nonlinear absorption will give rise to a distortion of the shape of the theoretical curve in the CA Z-scan by increasing the peak or valley [87]. However, here in Fig. 5, the curves are almost perfectly antisymmetric and the intensity of the peak is equivalent to that of the valley, which means a negligible effect of nonlinear absorption [86]. For solutions of the investigated fluorophores in CHCl_3 and THF, different powers were used in order to negate the detrimental effect of the nonlinear absorption [88].

The fitting of the data was done with the following equation:

$$T(z) \approx 1 - \frac{4\Delta\Phi_0 x}{(x^2 + 9)(x^2 + 1)} \quad (2)$$

where $x = \frac{z}{z_0}$, $z_0 = \frac{\kappa\omega_0^2}{2}$ is the beam diffraction length, ω_0 is the beam waist radius, κ is the wave vector of light, $\Delta\Phi_0$ is the phase shift at the focus, which is defined as $\Delta\Phi_0 = \kappa\Delta n L_{\text{eff}}$. Here $L_{\text{eff}} = \frac{1 - e^{-\alpha L}}{\alpha}$, in which L is the length of the sample and α is the linear absorption coefficient, $\Delta n_0 = \gamma I_0$ with I_0 being the irradiance within the sample approximately.

As the solvent and the solute both have a nonlinear optical response, we separate the contributions of solvent and solute to the solution nonlinearities using $n_2(\text{solution}) = (1-x)n_2(\text{solvent}) + xn_2(\text{solute})$, in which x is the molar fraction of the solute [89]. The calculated results are listed in Table 2. It can be seen that in the same solvent, with the conjugation length becoming larger, the n_2 value becomes larger too. This may be ascribed to the fact that the induced optical polarizability becomes stronger with increasing conjugation length [88].

As shown in Fig. 6, it is clear that for the same compound, in the

Table 2

Calculated results for n_2 (mean values for three times) of the four compounds and solvent^a.

Solvent	Compound	n_2 for solute (mean value, m^2W^{-1})	n_2 for solvent (mean value, m^2W^{-1})
CHCl_3	TBT	-1.43×10^{-12}	8.63×10^{-19}
	TVBVT	-1.20×10^{-12}	
	TSBST	-3.17×10^{-12}	
	TSVBVST	-1.12×10^{-11}	
THF	TBT	-9.02×10^{-13}	1.90×10^{-18}
	TVBVT	-9.72×10^{-14}	
	TSBST	-4.48×10^{-13}	
	TSVBVST	-1.24×10^{-12}

Fig. 6. The third-order nonlinear refractive coefficients of the four compounds in CHCl_3 (black line) and THF (red line); error bar included. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

solution of CHCl_3 , the n_2 value is almost one order of magnitude higher than the corresponding n_2 value in the solution of THF. For CHCl_3 and THF, their polarities are very close. That means that the solvent-solute nonspecific interaction [78] is not the main reason for the observed phenomenon. A possible explanation may be that the halogen-halide

interaction (B–F...Cl–C) enhances ICT characteristics of the four dyes in CHCl_3 and influences their nonlinear optical properties [30,75]. This indicates that not only the molecular structure influences the nonlinear optical properties of the compounds, but also the solvent-solute interaction plays an important role. From the values of the n_2 we can see that the four compounds are good NLO material candidates.

3. Experimental section

3.1. Materials and methods

All the reagents and solvents were purchased commercially and used without further purification unless specially stated. THF was dried over sodium, while DMF, CH_2Cl_2 and CHCl_3 were dried over CaH_2 and distilled before use. ^1H and ^{13}C NMR spectra were obtained on a Bruker Avance III 400 MHz. High resolution mass spectra (HRMS) were obtained on a Varian 7.0T FTMS, using a MALDI ionic source. UV–Vis absorption spectra were obtained on a SHIMADZU 1800 spectrophotometer. Fluorescence spectra for solutions were registered with a Hitachi F-2500 spectrophotometer. The concentrations of the solutions for absorption or emission spectra measurements were at $\sim 1 \times 10^{-6}$ M. The third-order NLO properties of the prepared complexes were measured by a CA Z-scan technique using a home-built setup with a femtosecond laser as the pump (pulse width 100 fs, wavelength 800 nm and repetition rate 82 MHz).

3.2. Synthetic procedures

The compounds **1**, **2**, **4**, **5** and **6** were synthesized using the methods described in the literature, and details can be found in the SI.

3.2.1. Synthesis of methyl 5-(4-(diphenylamino) phenyl) thiophene-2-carboxylate (**3**)

Under an argon atmosphere, the catalyst palladium diacetate (2.2 mg, 0.010 mmol) was added to a stirred mixture of (4-(diphenylamino) phenyl) boronic acid (0.29 g, 1.0 mmol), methyl 5-bromothiophene-2-carboxylate (0.28 g, 1.5 mmol) and potassium phosphate (0.43 g, 2.0 mmol) in 1.0 mL of water and 3.0 mL of isopropanol. The reaction mixture was stirred at 50 °C for 2 h. 5.0 mL of water was added to the mixture later to give a greenish grey powder. After column chromatography purification, the desired product was obtained as a greenish yellow powder (yield: 58%). ^1H NMR (400 MHz, CDCl_3) δ : 7.74 (d, J = 3.9 Hz, 1H), 7.51–7.46 (m, 2H), 7.32–7.25 (m, 4H), 7.19 (d, J = 3.9 Hz, 1H), 7.15–7.11 (m, 4H), 7.10–7.04 (m, 4H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ : 162.86, 151.47, 148.60, 147.26, 134.66, 130.88, 129.53, 127.08, 126.95, 125.03, 123.69, 122.95, 122.64, 52.22. HRMS m/z calcd. for $\text{C}_{24}\text{H}_{19}\text{NO}_2\text{S}$: 385.1136 $[\text{M}]^+$; obs. 385.1133.

3.2.2. Synthesis of **TBT**

Under an argon atmosphere, **2** (0.30 g, 1.0 mmol) and sodium hydride (0.12 g, 5.0 mmol) were added to a stirred solution of **1** in THF. The reaction mixture was refluxed overnight under inert atmosphere. After that, 1 M HCl was added to adjust the pH to be ~ 1.0 . After removal of the solvent and the addition of methanol, the mixture was kept in the refrigerator overnight to give the sediment.

The precipitate was dissolved in 10 mL of dichloromethane. Under the protection of argon, trimethylamine (0.20 mL, 0.40 mmol) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.50 mL, 4.0 mmol) were added. After being stirred for 2 h at room temperature, the solvent in the reaction mixture was removed under vacuum. A large amount of methanol was added, and then the mixture was kept in the refrigerator overnight to give the crude product. After column chromatography purification (300–400 mesh SiO_2 , CH_2Cl_2 :petroleum ether, 1:2.5), the product was obtained as magenta powder (yield: 53%). ^1H NMR (400 MHz, CDCl_3) δ : 7.97–7.88 (m, 4H), 7.41–7.32 (m, 8H), 7.23–7.16 (m, 12H), 7.01–6.95 (m, 4H), 6.88 (s, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ : 179.00, 153.74, 145.85, 130.54, 129.95, 126.61, 125.69, 123.53, 119.03, 91.09. HRMS m/z calcd. for $\text{C}_{39}\text{H}_{29}\text{BF}_2\text{N}_2\text{O}_2$: 606.2290 $[\text{M}]^+$; obs. 606.2290.

3.2.3. Synthesis of **TSBST**

The synthetic procedure of **TSBST** is the same as that of **TBT** except that **1** and **2** being replaced with **3** and **4**, respectively. The desired product was obtained as dark purple powder (yield: 31%). ^1H NMR (400 MHz, CDCl_3) δ : 7.95 (d, J = 4.2 Hz, 2H), 7.54–7.48 (m, 4H), 7.34–7.28 (m, 10H), 7.17–7.08 (m, 12H), 7.05 (d, J = 8.9 Hz, 4H), 6.67 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ : 173.33, 156.38, 149.66, 146.92, 135.71, 134.32, 129.70, 127.43, 125.73, 125.53, 124.28, 124.12, 122.13, 92.13. HRMS m/z calcd. for $\text{C}_{47}\text{H}_{33}\text{BF}_2\text{N}_2\text{O}_2\text{S}_2$: 770.2045 $[\text{M}]^+$; obs. 770.2045.

3.2.4. Synthesis of **TVBVT**

4-(diphenylamino) benzaldehyde (0.27 g, 1.0 mmol) and **6** (0.15 g, 1.0 mmol) were dissolved in 15 mL of toluene under inert atmosphere. Butylamine (0.07 g, 0.1 mmol) and tributyl borate (0.23 g, 0.10 mmol) was added to the system slowly under the protection of argon. The mixture was heated up to 60 °C and reacted for 12 h. After that, a large amount of methanol was added to the system. The mixture was transferred to the refrigerator to generate a black precipitate. The precipitate was purified by the column chromatography (300–400 mesh SiO_2 , CH_2Cl_2 :petroleum ether, 1:2) to give the product as an amaranth solid (yield: 34%). ^1H NMR (400 MHz, CDCl_3) δ : 7.95 (d, J = 15.4 Hz, 2H), 7.48–7.39 (m, 4H), 7.37–7.29 (m, 8H), 7.21–7.10 (m, 12H), 7.02–6.94 (m, 4H), 6.52 (d, J = 15.4 Hz, 2H), 5.96 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ : 178.76, 151.43, 146.52, 146.43, 130.83, 129.81, 126.92, 126.17, 124.99, 120.69, 117.48, 101.86. HRMS m/z calcd. for $\text{C}_{43}\text{H}_{33}\text{BF}_2\text{N}_2\text{O}_2$: 658.2603 $[\text{M}]^+$; obs. 658.2605.

3.2.5. Synthesis of **TSVBVST**

The synthetic procedure for **TSVBVST** is the same as the aforementioned process for **TVBVT** except that 4-(diphenylamino) benzaldehyde was replaced with **5**. The desired product was obtained as purple black powder (yield: 28%). ^1H NMR (400 MHz, CDCl_3) δ : 8.09 (dd, J = 15.0, 0.6 Hz, 2H), 7.51–7.46 (m, 4H), 7.37–7.33 (m, 2H), 7.33–7.27 (m, 8H), 7.24 (d, J = 3.9 Hz, 2H), 7.18–7.01 (m, 16H), 6.40 (d, J = 15.0 Hz, 2H), 5.94 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ : 178.11, 151.36, 148.97, 147.11, 139.23, 138.26, 136.16, 129.62, 127.13, 126.53, 125.29, 124.00, 123.93, 122.56, 118.29, 102.26. HRMS m/z calcd. for $\text{C}_{51}\text{H}_{37}\text{BF}_2\text{N}_2\text{O}_2\text{S}_2$: 822.2358 $[\text{M}]^+$; obs. 822.2358.

4. Conclusions

In summary, we have synthesized four difluoroboron β -diketonate compounds with different conjugation lengths. These four D- π -A molecules show strong absorption in the range of 400–750 nm which can be ascribed to the ICT process. All of them show positive solvatochromism. With the increasing polarity of the solvent, the maxima of the absorption and emission spectra show red shifts and the Stokes shift becomes larger. In toluene, the four compounds show a moderate to high relative quantum yield, more than 0.50. The multilinear analysis shows that the dipole-dipole nonspecific interactions play a main role in the solvato-chromism of these chromophores in different solvents. In the solutions of the four compounds in CHCl_3 , the halogen-halide interaction may influence the ground states of the molecules and thus induce the observed red shift of the absorption and emission spectra. Through the Z-scan measurements for the four compounds, we got their nonlinear refractive coefficients, which indicates that they are good candidates for nonlinear optical materials. We also found that the solvent-solute interaction, here to be halogen-halide interaction, influences the third-order nonlinear response in the solution of CHCl_3 of the four chromophores. It may provide a new strategy to the design of third-order NLO materials: the molecules could be designed

intentionally to use the interaction between the solvent and the materials to enhance the third-order NLO properties of the materials.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.dyepig.2018.11.002>.

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