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D- $\pi$ -A- $\pi$ -D type solvatochromic fluorescence probes based on triphenylamine: Synthesis,

#### **Photophysical properties and Application**

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#### **ABSTRACT:**

Two D– $\pi$ –A– $\pi$ –D type solvatochromic fluorescence probes (**JT1** and **JT2**) based on triphenylamine have been synthesized. The photophysical and electrochemical properties of these probes as well as their solvatochromic behavior were studied. The Stokes shifts of **JT1** and **JT2** reach 175 nm (6417.0 cm<sup>-1</sup>) and 218.6 nm (9916.7 cm<sup>-1</sup>) in the acetonitrile solution, respectively. There is an excellent linear correlation between the Stokes shifts and the E<sub>T</sub> (30) solvent polarity values in different solvents. The high responsiveness of **JT1** and **JT2** to solvent polarity makes them promising candidates for solvatochromic fluorescence probes, especially for the detection of the polarity of non-proton solvents or the content of water in tetrahydrofuran.

Keywords: Triphenylamine; Solvatochromic; Fluorescence probe; Polarity; Water

#### 1. Introduction

Generally, solvatochromic dyes possess a D– $\pi$ –A conjugated structure, which is composed of an electron donor, a  $\pi$ -spacer, and an acceptor. When such molecules are stimulated by light, intramolecular charge transfer (ICT) may occur between the electron donor and the electron acceptor [1-3]. Simultaneously, the fluorescence spectrum of these molecules is greatly affected by the polarity of solvents so that it is easy to exhibit solvatochromic phenomenon [4-13], which makes these molecules have a promising future in the application of polarity-sensitive fluorescent

probes. In the past decades, various organic solvent-sensitive probes with one-dimensional D– $\pi$ –A structure have been reported which exhibit negative or positive solvatochromism, mainly including Aladan [14], Neutral Red [15], Prodan [16], Nile Red [17], Pyrene [18], and their derivatives. Compared with the traditional one-dimensional D– $\pi$ –A framework molecules, the D– $\pi$ –A– $\pi$ –D structure molecule contains two donor moieties, which is more conducive to ICT as well as able to reduce the bandgap of molecular energy level, thus causing a red-shift of the spectrum [19]. Therefore, more and more attention has been paid to this type of molecules, which have been widely used in OLEDs [20], organic solar cells, and dye-sensitized solar cells [21-23]. However, research on such molecules as the polarity probe is still scarce, and some of them are not suitable for practical application because of their complex structures and difficult synthesis.

Based on the above considerations, a kind of novel molecules with  $D-\pi-A-\pi-D$  skeleton have been designed. On the one hand, a single carbonyl group is chosen as an acceptor unit originating from its non-linear bond angle can help to increase the polarity of the molecule, thereby increasing the sensitivity to solvent response. On the other hand, to avoid instability of the fluorescence spectrum caused by molecular aggregation, the propeller-type triphenylamine unit is selected as the donor. Besides, a non-polar benzene ring and a polar thiophene ring are used as bridging structures, respectively, to investigate further the effect of the  $\pi$ -bridge unit on the molecular properties. Finally, two simple solvatochromic dyes **JT1** and **JT2** were synthesized, and their photophysical and electrochemical properties were investigated in detail. The results show that they are susceptible to the polarity of the environment and can be employed to detect the polarity of aprotic solvents and the water content of organic solvents. Compared with **JT1**, the Stokes shifts of the probe **JT2** utilizing benzene ring as the  $\pi$ -bridge exhibit more variation with the polarity of solvents, and the detection sensitivity of **JT2** is higher than that of **JT1**.

#### 2. Experimental section

#### 2.1. Apparatus

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> using a Bruker Avance 600 MHz

spectrometer with TMS as internal reference. The IR spectra were measured on a Bruker V70 Infrared Spectrometer (Bruker Corporation). Mass spectra were obtained using an Orbitrap analyzer spectrometer (Thermo Electron Corporation). The melting points were taken on XT4B microscopic melting point apparatus and uncorrected. UV–Vis absorption spectra and fluorescence spectra were measured on a Shimadzu UV-3600 Plus spectrophotometer and a Hitachi F-4600 fluorescence spectrophotometer at the concentration  $1 \times 10^{-5}$  M solution. Electrochemical redox potentials ( $10^{-3}$  M) were investigated by Cyclic Voltammetry (CV) on a Modulab XM electrochemical workstation.

#### 2.2. Materials and reagents

The *N*, *N*-dimethylformamide (DMF) solvent used in the synthesis was pretreated with 4A molecular sieve. The tetrahydrofuran (THF) solvent was refluxed with sodium metal in an argon atmosphere before use, then cooled and stored in sealed containers for reserve. Bis(4-bromophenyl)methanone (4) and other reagents were obtained from Aldrich and were used without further purification.

#### 2.3. Synthesis of JT1 and JT2

#### 2.3.1. Synthesis of bis(5-(4-(diphenylamino)phenyl)thiophene-2-yl)methanone (JT1)

Bis(5-bromothiophen-2-yl)methanone (3) was synthesized by the reported method [24]. mp: 119-120 °C (literature data:119 °C).

HRMS (ESI, m/z):  $[M + H]^+$  calcd for  $[C_9H_5OBr_2S_2]^+$ :350. 8143, found: 350.8138.

Bis(5-bromothiophen-2-yl)methanone (3) (1.86 g, 5.28 mmol), 4-(diphenylamino)phenylboro-

nic acid (1.52 g, 5.28 mmol), and tetrakis(triphenylphosphine)palladium (0) (0.302 g, 0.261 mmol) were dissolved in dry THF (50 mL), then 2 M K<sub>2</sub>CO<sub>3</sub> aqueous solution (10.5 mL, 21 mmol) was added. The mixture was heated to reflux for 16 h under argon. After the mixture was cooled to ambient temperature, the reaction mixture was poured into water and extracted with  $CH_2Cl_2$ . The organic phase was washed with saturated NaCl solution, dried over anhydrous MgSO<sub>4</sub>, and then filtered. Evaporation of the solvent was carried out under reduced pressure. Crude product was purified by chromatography on silica gel using petroleum ether as eluent and dried under vacuum to afford an orange-red solid (**JT1**) in 13.9% yield (500 mg). mp:107–108 °C.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ ppm 7.87 (d, *J* = 4.2 Hz, 2H), 7.55–7.53 (m, 4H), 7.31–7.27 (m, 10H), 7.15–7.14 (m, 8H), 7.10–7.07 (m, 8H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ ppm 177.99, 152.57, 148.87, 147.26, 140.80, 134.16, 129.58, 127.24, 126.84, 125.18, 123.83, 122.88, 122.84. IR(KBr), v, cm<sup>-1</sup>:1589.31, 1436.93, 1282.63, 696.29.

HRMS (ESI, m/z):  $[M + H]^+$  calcd for  $[C_{45}H_{33}N_2OS_2]^+$ : 681.2029, found: 681.2030.

2.3.2. Synthesis of bis(4'-(diphenylamino)-[1,1'-biphenyl]-4-yl)methanone (JT2)

JT2 was synthesized according to the literature [25].

mp: 253–254 °C(literature data: 249- 250 °C); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ ppm 7.90 (d, *J* = 7.8 Hz, 4H), 7.69 (d, *J* = 8.4 Hz, 4H), 7.54 (d, *J* = 8.4 Hz, 4H), 7.31–7.28 (m, 8H), 7.16 (d, *J* = 7.2 Hz, 12H), 7.08–7.06 (m, 4H).

HRMS (ESI, m/z):  $[M + H]^+$  calcd for  $[C_{49}H_{37}ON_2]^+$ : 669.2900, found: 669.2888.

#### 3. Results and discussion

#### 3.1. Synthesis and characterization

The Synthetic routes of bis(5-(4-(diphenylamino)phenyl)thiophene-2-yl)methanone (**JT1**) and bis(4'-(diphenylamino)-[1,1'-biphenyl]-4-yl)methanone (**JT2**) are depicted in Scheme 1. **JT1** and **JT2** were synthesized by Suzuki–Miyaura cross-coupling reaction. The new compounds were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR and HRMS spectra (Figs. S1–S5).

#### Scheme 1

#### 3.2. Optical Properties

The maximum absorption wavelength and emission wavelength of **JT1** and **JT2** in various solvents are listed in Table 1. The UV–Vis absorption and fluorescence emission spectra of **JT1** and **JT2** in different solvents of various polarities are shown in Fig. 1 and Fig. 2. The results show that the absorption and emission properties of two molecules can be adjusted by changing the type of the  $\pi$ –bridge between triphenylamine and carbon-oxygen double bond.

As shown in Table 1 and Fig. 1, **JT1** and **JT2** exhibit broad absorption peaks in the wavelength range of 350–500 nm as well as exhibit relatively high molar extinction coefficients in different solvents, which may be attributed to the  $\pi$ - $\pi$ \* transitions in the intramolecular conjugated system. It is worth noting that the solvatochromic shift of absorption spectra is small, which indicates that the solvent polarity has little effect on the charge transfer of ground-state molecules due to a relatively small dipole moment. Besides, compared with **JT2**, due to the smaller dihedral angle between the carbonyl group and the  $\pi$ -bridge in **JT1**, a red-shift of about 50 nm is exhibited in the absorption spectrum [26].

#### Table 1

#### Fig. 1

Unlike the absorption spectrum, the solvatochromic shifts of the fluorescence spectra of JT1

and JT2 are very significant (Fig. 2). Firstly, the emission maxima of them have a significant bathochromic shift with increasing solvent polarity. In non-polar hexane, the emission maximums for JT1 and JT2 are 470 and 413 nm, respectively, while in polar DMSO, are 622 and 601 nm respectively, corresponding to a red-shift of 152 or 188 nm. Secondly, the spectral width of their fluorescent peak becomes wider with increasing solvent polarity, as shown in Fig. 2, the threshold extended from 172 to 314 nm or 175 nm to around 325 nm for JT1 and JT2, respectively. Thirdly, with increasing solvent polarity, the fluorescent colors of their solutions gradually change from blue to orange under ultraviolet irradiation. The above experimental results show that JT1 and JT2 have strong solvatochromic characteristics, and evident red-shift phenomenon (i.e., positive solvatochromism) can be observed (Fig. 3). The relevant mechanism may be that the  $\pi$ - $\pi$ \* electronic transition occurs when JT1 or JT2 is excited, which leads to the dipole moment of the excited states larger than that of the ground state. Consequently, the dipole-dipole force derived from the solvent-solute interactions also enhances as the polarity of the solvent increases and reduces the energy of the excited state, thus facilitating the intramolecular charge transfer. Compared to JT2, the emission wavelength of JT1 in the same solvent is red-shifted (Table 1) as a result of the thiophene  $\pi$ -bridge of **JT1** induces a highly polar twisted intramolecular charge transfer (TICT) state [27]. As expected, the TICT state of **JTI** makes it exhibit higher stability and longer emission wavelength than JT2 in polar solvent.

### Fig. 2

#### Fig. 3

#### 3.3. Stokes Shift in Different Solvents

The significant Stokes shift can avoid the interference produced by the excitation light and

scattered light, as well as the fluorescence intensity that is reduced by self-absorption, thereby improving the response sensitivity of fluorescent molecules [28]. To further understand the effects of solvent on the luminescence properties of these compounds, the Stokes shifts of JT1 and JT2 in different solvents were measured (Table 1). Excitingly, the Stokes shifts of the probes  $JT1 \sim 2$  in the polar solvent acetonitrile reach 175 and 218.6 nm, respectively. Moreover, there is a fine linear correlation (r > 0.99) between the Stokes shifts of **JT1~2** and the empirical polarity parameter E<sub>T</sub> (30) data [29] (Fig. 4) in the aprotic solvent. The linear regression equations are y = 8.88196x – 228.44316 (r = 0.9947) and y = 12.35532 x - 341.26254 (r = 0.9955) respectively. The slope of JT2 is greater than JT1, indicating that JT2 has a stronger solvatochromic response than that of JT1. Undoubtedly, this reason for the difference in solvent sensitivity is mainly due to the difference in the  $\pi$ -bridge and the electron polarizability of molecules. The above results demonstrate that the maximum emission peaks of JT1~2 depend on the polarity of solvents. We believe that the main reason for this phenomenon may be due to the strong charge transfer in the system, and the dipole interaction between solvent molecules and solute molecules is the main factor arising the stokes shift in fluorescence spectra of compounds.

#### Fig. 4

#### 3.4. Spectra in Mixed Solvents

To further prove the solvatochromic phenomenon of **JT1** and **JT2**, we selected two kinds of miscible solvents: strong polar solvent acetonitrile and weak polar solvent THF. We tested the absorption and fluorescence emission spectra of **JT1** and **JT2** in different ratio of THF and acetonitrile solvents. As a result, the absorption spectra of the two probes show little change (Fig. S6), which is consistent with the results shown in Figure 1a. It can be seen from Fig. 5 and Fig.6

that the fluorescence emission peaks red-shift gradually with increasing acetonitrile volume fraction and solvent polarity. The emission maxima for **JT1** and **JT2** are 546 and 500.6 nm in THF, 617 and 592.6 nm in acetonitrile corresponding to a red-shift of 71 and 92 nm, respectively. Besides, its fluorescence emission intensity is gradually weakened, and the single-photon fluorescence emission intensity in THF is about five times that in acetonitrile, which is a typical ICT effect. These phenomena are consistent with the phenomena of **JT1** and **JT2** in different solvents, which further proves that **JT1** and **JT2** have solvatochromic characteristics.

# Fig. 5

### Fig. 6

#### 3.5. Theoretical calculation and electrochemical properties of JT1 and JT2

By studying the absorption and fluorescence spectra of **JT1** and **JT2** molecules in different solvents, it can be seen that these two molecules have significant charge transfer characteristics in the excited state. To further understand this phenomenon, the density functional theory (DFT) calculations were performed using the Gaussian 09 program suite at the B3LYP/6-31 G(d) basis set (Fig. 7).

#### Fig. 7

It can be seen that in the optimized **JT1** and **JT2** structures, the dihedral angles of  $\pi$ -bridge and carbonyl are 15.58° and 25.46°, respectively, and the torsional angles of  $\pi$ -bridge and triphenylamine are 24.09° and 34.84°, respectively. The thiophene spacer on **JT1** exhibits a little less twisted structure, which enables the whole molecule to form a more effective  $\pi$ -conjugated system. From the isodensity plot of the frontier molecular orbitals of the two probes, the density of HOMO electron cloud is mainly distributed in the structure of triphenylamine, while the density of

LUMO electron cloud is mainly distributed in  $\pi$ -bridge and carbonyl, and the closer to the carbonyl group, the higher the electron cloud density. The calculation results show that the dye molecules can undergo significant electron cloud migration from electron donors to electron acceptors after being excited. Compared with the bandgap of **JT2** ( $\Delta E_g = 3.27 \text{ eV}$ ), the bandgap of **JT1** ( $\Delta E_g = 2.94 \text{ eV}$ ) becomes much narrower, which is the main reason that the absorption spectrum of **JT1** is red-shifted than that of **JT2**.

CV measurements were run in a solution of tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) in DMF with the addition of ferrocene as the internal standard. An Ag/AgCl (saturated) couple and a platinum wire were utilized as reference and counter electrodes, respectively, while a glassy carbon electrode was used as a working electrode. The HOMO and LUMO level of **JT1** and **JT2** can be estimated by CV according to the following equation (1) [30]:

$$HOMO = -[E_{ox} - E_{Fc/Fc+} + 4.8]eV$$

$$LUMO = HOMO + E_g \qquad \qquad \qquad E_g = 1240/\lambda_{onset} \qquad (1)$$

Optical energy gaps were determined from the UV–Vis absorptions in their Hexane solutions. As shown in Fig. S7, the ionization potential (HOMO levels) of **JT1** and **JT2** are -5.40 eV and -5.36 eV, respectively. The estimated electron affinity (LUMO levels) values for **JT1** and **JT2** are -2.74 eV and -2.30 eV, respectively.

It can be seen from the results that although the HOMO level of **JT1** has decreased compared with **JT2**, the decrease is not significant (~ 0.04 eV). Therefore, the role of the thiophene ring is mainly to reduce the LUMO level of the molecule (~ 0.40 eV), thus narrowing the bandgap of the molecule level and making the absorption spectrum a red-shift.

#### 3.6. Application of probe

Water is the most common impurity in various organic solvents. For many sensitive chemical reactions, water moisture in organic solvents plays a decisive role in the success of the experiment [31]. Therefore, the development of a simple fluorescent probe for the detection of water content in organic solvents has significant practical value. Since **JT1** and **JT2** are sensitive to solvent polarity, to further study the properties and application value of probes **JT1** and **JT2**, the absorption spectra (Fig. S8) and fluorescence intensity (Fig.8) of THF with different water content were measured in this experiment.

#### Fig. 8

Experiments show that the absorption spectra of **JT1** and **JT2** remain unchanged with the increase of water content in tetrahydrofuran, but the fluorescence intensity gradually decreases, and the maximum emission wavelength has a red-shift. The main reason for this phenomenon is that the polarity of the system increases gradually with the addition of water, and the increasing of polarity is beneficial to the intramolecular charge transfer, resulting in the change of the fluorescence spectrum. For **JT1**, when the volume fraction of water in tetrahydrofuran increases from 0 to 10.00%, the fluorescence intensity decreases rapidly from 1625 to 269.9. When the volume fraction of water increases from 10.00% to 60.00%, the fluorescence intensity decreases rapidly from 1625 to 269.9. When the volume fraction of water increases from 269.9 to 60.92. Based on this, further titration experiments were carried out in tetrahydrofuran with a gradual increase of water content from 0 to 10.00% (Fig. 9).

#### Fig. 9

Fitting the fluorescence spectra of probes **JT1** and **JT2** in tetrahydrofuran solution with different water content, we found that **JT1** had an excellent linear relationship when the water content is less than 1%, the corresponding linear equation is y = -504.10108x + 1588.79412, the linear correlation coefficient r = 0.99614. Similarly, when the water content is less than 1.5%, **JT2** also had an excellent linear relationship, the corresponding linear equation is y = -1810.8757x + 4020.10762, linear correlation coefficient r = 0.99601 (Fig. 10). It can be seen that as a fluorescent

probe molecular for detecting water in THF, **JT2** is more sensitive, and the detection range is wider than **JT1**.

### Fig. 10

### 4. Conclusion

In summary, two D– $\pi$ –A– $\pi$ –D type small organic molecules with the same core and carbonyl acceptor have been successfully synthesized as solvent polarity sensitive probe. The polarity determination of thirteen organic solvents and the detection of trace water in tetrahydrofuran were successfully carried out. The results indicated that two compounds have strong solvatochromic characteristics and large Stokes shifts, which can be used to detect the polarity of unknown non-proton solvents and trace water in tetrahydrofuran. Compared with the reported probe molecules, this novel D– $\pi$ –A– $\pi$ –D type small organic molecules with high sensitivity and simple structure might be a promising research direction of solvent polarity sensitive probe in the environment. In particular, in different solvents, the maximum absorption wavelength and the maximum emission wavelength of **JT1** are located in the visible region, which is very beneficial for applications in the field of biological research.

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### **Figure Captions**

Scheme 1. Synthetic routes of JT1 and JT2

Fig. 1 Normalized absorption spectra of JT1(a) and JT2(b) in different solvents.

**Fig. 2.** Normalized emission spectra of **JT1**(a) and **JT2**(b) in different Solvents, obtained under excitation at the maximum absorption wavelength in each solvent.

Fig. 3. The visual photographs of JT1 and JT2 in different solvents taken under visible light and365 nm UV (from a hand-held UV lamp) irradiation at room temperature with the concentration

of  $1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ .

Fig. 4. Correlation of Stokes shifts with  $E_T(30)$  for JT1 and JT2.

Fig. 5. Fluorescence spectra of JT1(a) and JT2(b) in different ratio of THF and acetonitrile solvents.

Fig. 6. The visual photographs of JT1 and TJ2 in different ratio of THF and acetonitrile solvents taken under visible light and 365 nm UV (from a hand-held UV lamp) irradiation at room temperature with the concentration of  $1.0 \times 10^{-5}$  mol·L<sup>-1</sup> (THF/Acetonitrile =  $10/0 \rightarrow 0/10$ ).

**Fig. 7.** Geometrical configuration of **JT1** and **JT2** and electron distribution of the HOMO and LUMO energy levels.

Fig. 8. Fluorescence spectra of JT1(a) and JT2(b) in different ratio of THF and water solvents.

**Fig. 9.** Fluorescence titration spectra of **JT1**(a) and **JT2**(b) in THF with water content from 0 to 10.00%.

Fig. 10. Plot of the fluorescence intensity of JT1 and JT2 in different water fractions.

NO.	Solvent	E <sub>T</sub> (30) (Kcal •	JT1						JT2					
		mol <sup>-1</sup> )	log ε	$\lambda^{abs}_{ m max}$	$\lambda^{em}_{ m max}$	Stokes shift	F	Φ	log ε	$\lambda^{abs}_{ m max}$	$\lambda_{\max}^{em}$	Stokes shift	F	Φ
				(nm)	(nm)	(nm)				(nm)	(nm)	(nm)		
1	Hexane	31.0	4.8738	423	470	47	3754	0.38	4.6395	369	413	44	296	0.02
2	$CCl_4$	32.5	4.5809	437	500	63	2583	0.22	4.6335	377	438.8	61.8	1515	0.19
3	Toluene	33.9	4.8089	438	506	68	3176	0.33	4.6284	378	450.6	72.6	3418	0.32
4	Ether	34.5	4.6325	434	516	82	1809	0.18	4.6937	371	463.4	92.4	4609	0.48
5	1,4-Dioxane	36.0	4.7896	437	518	81	2867	0.22	4.6702	375	467.8	89.6	4240	0.45
6	THF	37.4	4.8035	439	546	107	1949	0.19	4.5599	375	500.6	125.6	3597	0.38
7	EA	38.1	4.7459	434	544	110	1914	0.18	4.6656	372	504.4	132.4	3007	0.42
8	CHCl <sub>3</sub>	39.1	4.5465	452	574	122	793	0.13	4.6149	382	520	138	3119	0.45
9	DCM	40.7	4.7589	447	581	134	1394	0.14	4.6243	380	545.2	165.2	2200	0.22
10	Acetone	42.2	4.8028	439	590	150	832	0.10	4.5599	373	551.2	178.2	695	0.09
11	DMF	43.2	4.7796	449	608	159	430	0.03	4.5378	380	576.2	196.2	364	0.02
12	DMSO	45.1	4.738	455	622	167	224	_	4.5809	383	601	218	81	_
13	MeCN	45.6	4.786	442	617	175	176	0.03	4.6385	374	592.6	218.6	132	0.01

Table 1. Photophysical properties of JT1 and JT2 in different solvents and  $E_T(30)$  values of solvents.

log ɛ: Log of the molar extinction coefficient at  $\lambda_{\max}^{abs}$ .

F: Fluorescence intensity at  $\lambda_{\max}^{em}$ .

 $\Phi$ : Fluorescence quantum yield. Quantum yields were determined by using quinine sulfate ( $\Phi = 0.54$  in 0.1 M H<sub>2</sub>SO<sub>4</sub>) as a standard.

Declaration of competing interests

We declare no competing financial interest.

# **Credit Author Statement**

**Zhen-E Chen:** Conceptualization, Methodology, Resources, Writing- Reviewing and Editing. **Qiang-long Qi:** Investigation, Supervision.

Hai Zhang: Conceptualization, Investigation, Resources.

Solution

### Graphical abstract

### Highlights:

1. Synthesis of two simple D- $\pi$ -A- $\pi$ -D type solvatochromic fluorescence probes with the same

core and carbonyl acceptor.

2. The Stokes shifts of the probes have an excellent linear relationship with the  $E_{T}\left( 30\right)$  in different

solvents (r > 0.99).

3. The probes were sensitive to the change of the polarity of non-proton solvents.

4. The probes can be applied for detecting the trace water content in tetrahydrofuran solution.

Solution