Position of Biphenyl Group Turning The Structure and Photophysical Property of D- π - π -A Prototype Fluorescent Material

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**Position of biphenyl group turning the structure and
photophysical property of D- π - π -A prototype fluorescent
material**

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Abstract: Three novel D- π - π -A prototype compounds, namely, (E)-2-(3-([1,1'-biphenyl]-2-yl)-1-(9H-fluoren-2-yl)allylidene)malononitrile (2-BAM), (E)-2-(3-([1,1'-biphenyl]-3-yl)-1-(9H-fluoren-2-yl)allylidene)malononitrile (3-BAM), (E)-2-(3-([1,1'-biphenyl]-4-yl)-1-(9H-fluoren-2-yl)allylidene)malononitrile (4-BAM) were synthesized. Furthermore, the structures and photophysical properties of three compounds were compared. Molecules of 2-BAM were packed into a 1D column structure with H-aggregation. However, both of 3-BAM and 4-BAM were packed into 3D layer structures with J-aggregation, respectively. Although three compounds all showed highly twisted molecular geometries, their molecular packing and intermolecular interactions were different. Because of the differences in electronic structures of molecules, the three compounds displayed different emission behaviors in solid and dilute solution. This study indicated that changing the position of biphenyl groups is an effective way to turn the structures and photophysical properties of such D- π - π -A prototype fluorescent material.

Key words: biphenyl, structure, photophysical property

Introduction

Due to the excellent characteristics and wide use in the fields of chemiluminescence, bioimaging, and lighting devices, a number of donor-acceptor (D-A) substituted π -conjugated organic fluorescent materials (D- π -A) have been synthesized and studied[1,2,3,4,5]. Previous studies have shown that, as for D- π -A prototype fluorescent material, subtle variation of molecular structure would give rise to change of their photophysical properties [6,7,8,9,10]. However, in order to further understand the structure-property relationship of organic fluorescent materials, studies on D- π -A prototype organic fluorescent materials are still isolated event. Therefore, there is a high demand for exploring new types of organic fluorescent materials.

In this paper, we have designed and synthesized three novel D- π - π -A prototype organic fluorescent materials by changing the positions of biphenyl groups, namely, (E)-2-(3-([1,1'-biphenyl]-2-yl)-1-(9H-fluoren-2-yl)allylidene)malononitrile (2-BAM), (E)-2-(3-([1,1'-biphenyl]-3-yl)-1-(9H-fluoren-2-yl)allylidene)malononitrile (3-BAM), and (E)-2-(3-([1,1'-biphenyl]-4-yl)-1-(9H-fluoren-2-yl)allylidene)malononitrile (4-BAM) (Scheme 1). Furthermore, their structures and photophysical properties were studied and compared. The results showed that changing

the position of biphenyl groups would affect the structures and photophysical property of such D- π - π -A prototype organic fluorescent materials, which is an effective way for turning structure and photophysical property of organic fluorescent materials.

Scheme 1. Synthetic route and chemical structures of three compounds

Experimental section

General

Chemicals and solvents were purchased from Aldrich and Acros without further purification. The three compounds in this study were synthesized by the Knoevenagel reaction in a satisfactory yield [11]. The synthesis routes of three compounds were shown in Scheme 1. The ^1H NMR and ^{13}C NMR spectra of three compounds were taken at 303K on a Agilent Technologies NMR spectrometer. Elemental analysis was performed using Flash EA 1112, CHNS-O instrument. The X-ray powder experiments were recorded on an 18 kW advance diffractometer (INCA Energy, Oxford Instruments). The differential calorimetry (DSC) was determined from 30 to 300 $^\circ\text{C}$ at 10 $^\circ\text{C}/\text{min}$ (Netzsch TG 209 apparatus). UV-vis absorption spectra were obtained on a TU-1901

spectrophotometer. Fluorescence spectra were taken on a RF-5000 spectrometer. The absolute photoluminescence quantum yield (Φ_{PL}) was determined by HORIBA FluoroMax-4P fluorescence spectrometer using an integrating sphere.

Diffraction data for crystal were obtained with a Rigaku RAXISRAPID diffractometer. The structures were solved with direct methods using the SHELX program and refined with fullmatrix least-squares procedure [12]. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were inserted at idealized positions and refined by isotropic displacement. The DIAMOND program [13] and Mercury [14] were used to obtain the molecular graphics. The Multiwfn 3.7 program [15] was used to obtain the distributions of HOMO and LUMO.

Synthesis

Synthesis of (E)-2-(3-([1,1'-biphenyl]-2-yl)-1-(9H-fluoren-2-yl)allyldene)malononitrile (2-BAM)

Initially, 2-acetylfluorene **1** (2.45 g, 11.75 mmol) was stirred with malononitrile (1.16 g, 17.625 mmol) in mixture of dichloromethane (20 mL) and methanol (10 mL), ammonium acetate (1.36 g, 17.625 mmol) was subsequently added. The mixture was stirred for 6 hours at 40°C. After removing the solvent, the resulting precipitate was separated with chromatography on silical gel (ethyl acetate/petroleum ether = 5/1) to afford pure compound **2** as a canary yellow solid (2.4g, 80%). Anal. Calcd. (%) : C, 84.77; H, 4.30; N, 10.93. Found: C, 84.71; H, 4.32; N, 10.97. ^1H NMR (300 MHz, CDCl_3): δ 7.90 (m, 2H), 7.66 (s, 1H), 7.62 (m, 1H), 7.64 (t, 2H, 6Hz), 7.44 (m, 2H), 4.00 (m, 2H), 2.72 (s, 3H). (Fig. S1, ESI †). ^{13}C NMR (300 MHz, CDCl_3): 173.28, 145.39, 144.52, 142.73, 141.28, 139.77, 128.39, 127.24, 126.36, 125.84, 120.92, 118.42, 116.58, 77.49, 37.02, 25.76.

Compound **2** (0.24 g, 0.92 mmol) was stirred with biphenyl-2-carboxaldehyde (0.17 g, 0.92 mmol) in 2-propanol (15 mL). A catalytic amount of piperidine was added to the solution, and then the mixture was stirred for 3 hours at 70°C. After removing the solvent, the resulting precipitate was separated with chromatography on silical gel (dichloromethane/methanol = 4/1) to give pure 2-BAM as a yellow solid. Yield: 0.31g (81%). Anal. Calcd. (%) : C, 88.54; H, 4.80; N, 6.66. Found: C, 88.57; H, 4.82; N, 6.61. ¹H NMR (300 MHz, CDCl₃): δ 7.80 (d, 1H, 3Hz), 7.75 (d, 1H, 6Hz), 7.58 (d, 1H, 3Hz), 7.48 (t, 2H, 18Hz), 7.46 (m, 2H), 7.45 (s, 1H), 7.42 (t, 2H, 6Hz), 7.39 (t, 1H, 3Hz), 7.35 (m, 3H), 7.17 (m, 3H), 7.06 (d, 1H, 12Hz), 3.84 (s, 2H) (Fig. S2, ESI⁺). ¹³C NMR (300 MHz, CDCl₃): δ 169.48, 145.72, 142.37, 141.69, 140.91, 136.73, 132.92, 131.77, 129.46, 128.28, 127.75, 126.58, 125.13, 124.96, 122.32, 121.69, 120.34, 116.68, 64.89, 37.38 ppm. IR (KBr pellet, cm⁻¹): 2285, 1589, 1514, 1467, 1452, 1425, 1396, 1330, 1261, 1199, 1153, 835, 763, 738, 696 (Fig. S3, ESI⁺).

Synthesis of (E)-2-(3-([1,1'-biphenyl]-3-yl)-1-(9H-fluoren-2-yl)allylidene)malononitrile (3-BAM)

This compound was synthesized by the same procedure as described for 2-BAM except that biphenyl-3-carboxaldehyde was used instead of biphenyl-2-carboxaldehyde. Anal. Calcd. (%) : C, 88.54; H, 4.80; N, 6.66. Found: C, 88.51; H, 4.78; N, 6.71. ¹H NMR (300 MHz, CDCl₃): δ 7.99 (d, 1H, 6Hz), 7.91 (d, 1H, 6Hz), 7.74 (m, 3H), 7.64 (m, 5H), 7.53 (d, 1H, 3Hz), 7.47 (m, 6H), 7.03 (d, 1H, 12Hz), 4.04 (s, 2H) (Fig. S4, ESI⁺). ¹³C NMR (300 MHz, CDCl₃): δ 168.31, 144.63, 141.82, 140.52, 139.78, 136.45, 131.92, 131.07, 130.27, 129.15, 127.39, 126.18, 125.96, 124.47, 120.59, 116.28, 64.14, 37.22 ppm. IR (KBr pellet, cm⁻¹): 2218, 1606, 1514, 1452, 1421, 1394, 1348, 1325, 1298, 1191, 1149, 1097, 1026, 968, 887, 831, 798, 765, 736, 702 (Fig. S5, ESI⁺).

Synthesis of (E)-2-(3-([1,1'-biphenyl]-4-yl)-1-(9H-fluoren-2-yl)allylidene)malononitrile (4-BAM)

This compound was synthesized by the same procedure as described for 2-BAM except that biphenyl-4-carboxaldehyde was used instead of biphenyl-2-carboxaldehyde. Anal. Calcd. (%) : C, 88.54; H, 4.80; N, 6.66. Found: C, 88.59; H, 4.79; N, 6.62. ^1H NMR (300 MHz, CDCl_3): δ 7.99 (d, 1H, 6Hz), 7.91 (d, 1H, 6Hz), 7.67 (m, 9H), 7.43 (m, 6H), 7.05 (d, 1H, 12Hz), 4.05 (s, 2H) (Fig. S6, ESI †). ^{13}C NMR (300 MHz, CDCl_3): δ 169.21, 144.56, 142.49, 140.11, 135.92, 132.31, 130.82, 129.59, 128.46, 127.49, 126.88, 126.24, 125.19, 124.36, 121.48, 116.83, 63.77, 36.25 ppm. IR (KBr pellet, cm^{-1}): 2218, 1597, 1552, 1504, 1409, 1328, 1191, 1151, 1089, 1004, 977, 948, 883, 835, 765, 727, 696, 765, 736, 702 (Fig. S7, ESI †).

Results and discussion

Photophysical properties in solid state

As shown in Fig.1, 2-BAM, 3-BAM, and 4-BAM displayed strong emissions with maximum PL peaks (λ_{max}) at 516, 522, and 567 nm, respectively (Fig.1 and Table 3). Under illumination with a 365 nm UV lamp, Solids of 2-BAM and 3-BAM both emitted strong yellow green light, while 4-BAM emitted strong yellow light. Compared with the solid of 2-BAM, the emission wavelength of 3-BAM was slightly red-shifted. However, the emission wavelength of 4-BAM was red-shifted with 51 nm, compared with that of 2-BAM (λ_{max} , 516 and 567 nm for 2-BAM and 4-BAM, respectively, Table 3). From the solid emission behaviors of three compounds, it can be found that changing the positions of biphenyl group would lead to different photophysical property of such organic fluorescent compound.

Fig. 1 The emission spectra of three compounds in solid state

Crystal structures

In order to investigate the structure-property relationship of three compounds, single crystals of the three compounds were obtained by the vapor diffusion method. Mixed solvents of dichloromethane and methanol were used for three compounds (dichloromethane/methanol; 3/1, 2/1, and 4/1 for 2-BAM, 3-BAM, and 4-BAM, respectively). Single crystals of three compounds were obtained by slow evaporation of the mixed solvents at room temperature for 4-5 days, respectively. Relevant crystallographic data of 2-BAM, 3-BAM, and 4-BAM are summarized in Table 1.

Crystal of 2-BAM have the space group $P\bar{1}$ with triclinic system, and its molecular illustration is shown in Fig. 2a. In the molecule of 2-BAM, the dihedral angle between the fluorene and conjugated bridge ($\text{C}=\text{C}(\text{CN})_2$)-conjugated bridge ($\text{C}=\text{C}$) moieties was 65.2° , and the dihedral angle between biphenyl and conjugated bridge ($\text{C}=\text{C}(\text{CN})_2$)-conjugated bridge ($\text{C}=\text{C}$) moieties was 9.6° (see Fig.2b). In addition, the dihedral angle between the two phenyl rings was 44.8° (see Fig. 2b). These dihedral angles indicate that molecular geometry of 2-BAM in solid state was highly twist. As shown in Fig.2c, molecule in 2-BAM slipped to the neighboring molecule, with a slip angle of 60.5°

and a vertical distance of 3.49 Å, which indicates the H-aggregation of molecules. The main interactions among the neighboring molecules in 2-BAM were C-H...N interactions (Table 2), and molecules were packed into a 1D column structure (Fig.2c). In addition, the centre distance d_{centre} between the neighboring molecules in 2-BAM was measured to be 4.0 Å, and vertical distance d_{vertical} between two fluorene moieties was 3.49 Å, indicating that there was relatively strong $\pi\cdots\pi$ stacking.

Fig.2 Perspective views of 2-BAM with the thermal ellipsoids set at 30% probability (a). Schematic molecular structures of 2-BAM in crystal. The fluorene moieties were shown in red. The conjugated bridge (C=C(CN)₂)-conjugated bridge (C=C) moieties were shown in blue. The phenyl rings linked to the conjugated bridge (C=C(CN)₂)-conjugated bridge (C=C) moieties were shown in light green. The phenyl rings on the other side of biphenyl moieties were shown in magenta (b). Packing diagram of 2-BAM via H-aggregation. The biphenyl moieties were shown in magenta (c).

Similar to that of 2-BAM, the unit cell of 3-BAM also has the space group $P\bar{1}$, belonging to triclinic system, and its molecular illustration is presented in Fig. 3a. In the molecule of 3-BAM, the dihedral angle between the fluorene and conjugated bridge (C=C(CN)₂)-conjugated bridge (C=C) moieties was 58.6°, and the dihedral angle between

biphenyl and conjugated bridge (C=C(CN)₂)-conjugated bridge (C=C) moieties was 9.8° (see Fig.3b). In addition, the dihedral angle between the two phenyl rings was 37.3°. These dihedral angles indicated that molecular geometry of 3-BAM in solid state was also highly twist. As shown in Fig.3c, molecule in 3-BAM slipped to the neighboring molecule, with a slip angle of 13.3° and a vertical distance of 2.38 Å, indicating the J-aggregation of molecules. The main interactions between the neighboring molecules in 3-BAM were C-H... π and C-H...N interactions (Table 2), and molecules were packed into a 3D layer structure (Fig.3d). In addition, the centre distance d_{centre} between the neighboring molecules in 3-BAM was measured to be 10.27 Å, and vertical distance d_{vertical} between two fluorene moieties was 2.38 Å (Fig.3c), indicating that there was no overlap between the neighboring fluorene moieties, and no π ... π interactions were formed in the crystal of 3-BAM.

Fig.3 Perspective views of 3-BAM with the thermal ellipsoids set at 30% probability (a). Schematic molecular structures of 3-BAM in crystal. The fluorene moieties were shown in red. The conjugated bridge (C=C(CN)₂)-conjugated bridge (C=C) moieties were shown in blue. The phenyl rings linked to the conjugated bridge (C=C(CN)₂)-conjugated bridge (C=C) moieties were shown in light green. The phenyl rings on the other side of biphenyl moieties were shown in magenta (b). Packing diagram of 3-BAM via J-aggregation. The biphenyl moieties were shown in magenta (c). The layer structure of 3-BAM (d). Hydrogen atoms are omitted for clarity.

The unit cell of 4-BAM was monoclinic, and the space group was $C_{2/c}$. The molecular illustration of 4-BAM was presented in Fig. 4a. In the molecule of 4-BAM, the dihedral angle between the fluorene and conjugated bridge ($C=C(CN)_2$)-conjugated bridge ($C=C$) moieties was 67.8° , and the dihedral angle between biphenyl and conjugated bridge ($C=C(CN)_2$)-conjugated bridge ($C=C$) moieties was 16.1° (see Fig.4b). In addition, the dihedral angle between the two phenyl rings was 35.6° (see Fig.4b). These dihedral angles indicated that molecular geometry of 4-BAM in solid state was also highly twist. As shown in Fig.4c, molecule in 4-BAM slipped to the neighboring molecule, with a slip angle of 48.6° and a vertical distance of $11.88 \text{ \AA}$ (see Fig.4c), indicating the J-aggregation of molecules. The main interactions between the neighboring molecules in 4-BAM were C-H... π and C-H...N interactions (Table 2), and molecules were packed into a 3D layer structure (Fig.4d). In addition, the centre distance d_{centre} between the two neighboring molecules in 4-BAM was measured to be $15.90 \text{ \AA}$, and vertical distance d_{vertical} between two fluorene moieties was $11.88 \text{ \AA}$, indicating that there was no overlap between the neighboring fluorene moieties, and no $\pi\cdots\pi$ interactions were formed in the crystal of 4-BAM.

From the crystal analysis of three compounds, it can be found that although all three compounds showed highly twisted geometries, their molecular packing and intermolecular interactions were different. Especially, their dihedral angles between the two phenyl rings were different (44.8° , 37.3° and 35.6° for 2-BAM, 3-BAM and 4-BAM, respectively), which indicates that changing the position of biphenyl group would affect the geometries of its own. Overall, the different molecular structures of three compounds indicated the influence induced by changing the position of biphenyl groups.

Fig.4 Perspective views of 4-BAM with the thermal ellipsoids set at 30% probability (a). Schematic molecular structures of 4-BAM in crystal. The fluorene moieties were shown in red. The conjugated bridge (C=C(CN)₂)-conjugated bridge (C=C) moieties were shown in blue. The phenyl rings linked to the conjugated bridge (C=C(CN)₂)-conjugated bridge (C=C) moieties were shown in light green. The phenyl rings on the other side of biphenyl moieties were shown in magenta (b). Packing diagram of 4-BAM via J-aggregation. The biphenyl moieties were shown in magenta (c). The stacking image of 4-BAM (d). Hydrogen atoms are omitted for clarity.

In order to study the influence induced by changing the positions of biphenyl groups, and further investigate the structure-property relationship of three compounds, the HOMOs and LUMOs of the three compounds in crystal were obtained by quantum computations at the molecular level according to the density functional method at the B3LYP/6-31G level. As shown in Fig.5, as for 2-BAM and 3-BAM, their HOMO electrons were both distributed mainly on conjugated bridge (C=C(CN)₂)-conjugated bridge (C=C) and fluorene moieties, respectively. However, the HOMO electrons of 4-BAM were distributed on the whole molecular backbone, which would lead to better conjugation character of molecules, thus giving rise to the red-shifted emission of 4-BAM, compared with that of 2-BAM and 3-BAM in solid state (λ_{max} ; 516, 522 and 567 nm for 2-BAM, 3-BAM, and 4-BAM, respectively, Table 3).

Thus, it can be found from the theoretical calculations that, changing the position of biphenyl group would affect electron distributions of three compounds in solid state, endowing them with different emission behaviors.

Fig.5 Calculated frontier molecular orbitals of three compounds in solid state

The UV-vis absorption of three compounds

The absorption spectra of three compounds in dichloromethane (DCM) were shown in Fig.6. There are two main absorption bands in such D- π - π -A prototype compounds (see Fig.6). As shown in Fig.6, as for the three compounds, there was one similar absorption located at about 229 nm (229, 229, and 228 nm for 2-BAM, 3-BAM, and 4-BAM, respectively), corresponding to the intramolecular charge transfer (ICT) process. However, the other absorptions located at about 365 nm were different (365, 369, and 385 nm for 2-BAM, 3-BAM, and 4-BAM, respectively, Table 3), which correspond to the $\pi \rightarrow \pi^*$ transition. From the absorption spectra of three compounds, it can be found that the absorption band contributed to $\pi \rightarrow \pi^*$ transition of 4-BAM was red-shifted compared with that of 2-BAM and 3-BAM. Therefore, the similarity and difference of absorption spectra in dilute solution indicate the influence on the

ground-state electron distributions of such fluorescent material induced by changing the positions of biphenyl groups.

Fig.6 Normalized absorption spectra of the isomers in DCM (10 μ M)

Table 1 Crystal data and structure refinements of isomers in this study

Compd	4-BAM	3-BAM	2-BAM
Formula	$C_{31}H_{20}N_2$	$C_{31}H_{20}N_2$	$C_{31}H_{20}N_2$
Formula weight	420.49	420.49	420.49
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$C2_c$	$P\bar{1}$	$P\bar{1}$
$a/\text{\AA}$	30.220(4)	9.0231(5)	9.0231(5)
$b/\text{\AA}$	9.8288(17)	10.6675(6)	10.6675(6)
$c/\text{\AA}$	18.078(2)	11.6695(7)	11.6695(7)
$\alpha/^\circ$	90	89.655(2)	89.655(2)
$\beta/^\circ$	122.012(9)	83.453(2)	83.453(2)
$\gamma/^\circ$	90	89.107(2)	89.107(2)
$V/\text{\AA}^3$	4553.1(12)	1151.48(15)	1115.76
Z	8	2	2
$D_{\text{calc}} (\text{Mg}/\text{m}^{-3})$	1.227	1.213	1.252
T/K	296(2)	296 (2)	296(2)
$\mu (\text{mm}^{-1})$	0.072	0.071	0.073
Cryst dimensions	$0.320 \times 0.260 \times 0.250$	$0.220 \times 0.180 \times 0.160$	$0.250 \times 0.230 \times 0.210$
No.of felns collected	28914	17970	17357
No. of unique reflns	5185	5283	5094
Goodness-of-fit on F^2	1.029	1.020	1.026
$R_1, wR_2 (I > 2\sigma(I))$	$R_1 = 0.0525, wR_2 = 0.1215$	$R_1 = 0.0526, wR_2 = 0.1134$	$R_1 = 0.0517, wR_2 = 0.1205$
R_1, wR_2 (all data)	$R_1 = 0.0861, wR_2 = 0.1383$	$R_1 = 0.1081, wR_2 = 0.1334$	$R_1 = 0.0886, wR_2 = 0.1366$
CCDC	2065607	2065609	2065615

Table 2 Summary of intermolecular interactions in crystal structures of three compounds

Compd	Interaction	d (Å)	A (°)
2-BAM	C22-H22...N1	3.50 ^a	148.93
	C7-H7...N2	3.14 ^a	160.95
3-BAM	C9-H9...N1	3.36 ^a	122.11
	C18-H18... π_1^b	3.16 ^c	120.81
	C26-H26... π_1^b	3.21 ^c	122.85
4-BAM	C10-H10...N1	3.55 ^a	145.79
	C14-H14... π_2^d	2.71 ^c	135.23

^aThe distances were measured from the hydrogen atom the nitrogen atom.

^b π_1 corresponds to the phenyl ring made by the carbon atoms of C7-C12.

^cThe distances were measured from the hydrogen atom to the center of phenyl ring.

^d π_1 corresponds to the phenyl ring made by the carbon atoms of C8-C13.

The photoluminescence (PL) property in solution

The photoluminescence property of three compounds in DCM was also investigated. As shown in Fig.7, the maximum PL peaks ($\lambda_{\max}$) of 2-BAM, 3-BAM, and 4-BAM were 518, 520, and 547 nm, respectively (Table 3). Compared with that of 2-BAM and 3-BAM, the emission wavelength of 4-BAM in dilute solution was red-shifted. In order to further investigate structure-property relationship of three compounds in dilute solution, the HOMOs and LUMOs of three compounds in solution state were also obtained by quantum computations at the molecular level, according to the density functional method at the B3LYP/6-31G level. For 2-BAM and 3-BAM, their HOMO electrons were both distributed mainly on conjugated bridge (C=C(CN)₂)-conjugated bridge (C=C) and fluorene moieties, respectively (see Fig.8). However, the HOMO electrons of 4-BAM were distributed through the whole molecular backbone, which would lead to better molecular conjugation character, thus giving rise to the red-shifted emission of 4-BAM in solution, compared with that of 2-BAM and 3-BAM ($\lambda_{\max}$; 518, 520 and 547 for

2-BAM, 3-BAM, and 4-BAM, respectively, Table 3).

Fig.7 The PL spectra of three compounds in DCM (10 μ M)

Fig.8 Calculated frontier molecular orbitals of three compounds in dilute solution

Table 3 Photophysical properties of isomers in this study

Compd	Solution		Solid	
	Abs(nm)	PL(nm)	PL(nm)	$\Phi_{PL}(\%)$
2-BAM	365	518	516	31
3-BAM	369	520	522	53
4-BAM	385	547	567	59

Thermodynamic property

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) of three compounds were taken to study their thermodynamic stability (Fig. S8, ESI†). As Fig. 9 shows, 2-BAM, 3-BAM, and 4-BAM melt at 210.05, 216.81, and 219.27 °C, respectively, indicating that the three compounds all exhibit high thermal stability. In addition, the similar melting points of three compounds reveal that changing the position of biphenyl group would not affect melting points of such fluorescent material distinctly. However, this is not the case for their melting enthalpy (4.88, 73.98, and 82.36 J g⁻¹ for 2-BAM, 3-BAM, and 4-BAM, respectively).

Fig.9 DSC profiles of three compounds

Conclusion

In order to study the influence on the structure and property of D- π - π -A prototype organic fluorescent material induced by the changing the position of biphenyl group, three novel compounds, namely, (E)-2-(3-([1,1'-biphenyl]-2-yl)-1-(9H-fluoren-2-yl)allylidene)malononitrile (2-BAM), (E)-2-(3-([1,1'-biphenyl]-3-yl)-1-(9H-fluoren-2-yl)allylidene)malononitri-

le (3-BAM), (E)-2-(3-([1,1'-biphenyl]-4-yl)-1-(9H-fluoren-2-yl)allylidene)malononitrile (4-BAM) were synthesized. Furthermore, their structure-property relationship were investigated. Although three compounds all showed highly twisted geometries in crystals, their molecular packing and intermolecular interactions were different. Especially, changing the position of biphenyl groups would give rise to different geometries of its own. Because of the differences in electronic structures, the three compounds displayed different emission behaviors in solid and dilute solution. This study indicates that changing the positions of biphenyl groups is a useful way for turning the structure and property of D- π - π -A prototype fluorescent material.

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Author Declarations

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Contributions

Dong-En Wu: conceptualization; investigation; methodology; formal analysis; writing-original draft. Qin-Yuan Yin: conceptualization; investigation; methodology; writing-review and editing; supervision. Qing-Hui Guo: writing-review and editing. All authors read and approved the final manuscript.

Ethical approval

The submitted manuscript are prepared in compliance with the Ethics in Publishing Policy as described in the Guide for Authors, the work described was original research that has not been published previously, and not under consideration for publication elsewhere, in whole or in part.

Conflict of interest

The authors declare that they have no conflict of interest.

Consent to participate

All the co-authors consent to participate.

Consent for publication

All the co-authors consent to publish.

Data availability

All the data were given in the manuscript and supporting information files.

Code availability

Not applicable

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