Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers. This journal is © the Partner Organisations 2020

# **Electronic Supplementary Information**

Tuning the optical properties of N-aryl benzothiadiazole via Cu(II)-catalyzed intramolecular C-H amination: the impact of molecular feature on aggregation and solid luminescence

Yingnan Zhao,<sup>a</sup> Jie Ding,<sup>\*a</sup> Xiao Han,<sup>b</sup> Ting Geng,<sup>c</sup> Xiuwen Zhou,<sup>d</sup> Chen Hu,<sup>a</sup> Yashu, Wang,<sup>a</sup> Guanjun Xiao,<sup>\*c</sup> Bo Zou,<sup>c</sup> and Hongwei Hou <sup>\*a</sup>

<sup>a</sup> College of Chemistry, Zhengzhou University, Henan 450001, China.

<sup>b</sup> College of Chemical Engineering & Material, Handan University, Hebei, 056005, China.

- <sup>c</sup> State Key Laboratory of Superhard Materials, College of Physics, Jilin University, Changchun 130012, China.
- <sup>d</sup> School of Mathematics and Physics, The University of Queensland, Brisbane, Queensland 4072, Australia.

E-mail: jieding@zzu.edu.cn

E-mail: houhongw@zzu.edu.cn

E-mail: xguanjun@jlu.edu.cn

### **Experimental Section**

### Materials.

All chemicals and solvents were purchased from commercial sources and used without further purification.

### Measurements.

The <sup>1</sup>H NMR spectra were recorded on a 600 MHz NMR Spectrometer (AVIII HD 400/AVIII HD 400). The elemental analyses were performed with FLASH EA 1112 elemental analyzer. Powder X-ray diffraction (PXRD) patterns were recorded on Cu K $\alpha_1$  radiation on a PANalyticalX'Pert PRO diffractometer. Thermal analyses were carried out on a Netzsch STA 449C thermal analyzer at a heating rate of 10 °C min<sup>-1</sup> in air. Mass spectra (MS) were recorded on a Bruker Esquire 3000 plus ion trap mass spectrometer (Brucker-Franzen Analytik GmbH, Bremen, Germany). UV-Vis absorption spectra were obtained from a JASCO FP-8300 UV/Vis Spectrophotometer at room temperature. The measurements of steady-state emission spectra were conducted on a JASCO FP-8300 fluorescence spectrophotometer at room temperature. The relative quantum yield of emission in sample was by the optical dilute method<sup>1</sup> with rhodamine B EtOH solution ( $\Phi_r = 0.65$ ) as the standard<sup>2</sup>. The absolute quantum yield and lifetime of emission were detected with a photoluminescence quantum yield measurement system (Edinburgh Instruments Ltd FLS980 Fluorescence Spectrometer, the fluorescence lifetime measurement range is 100 ps ~ 50 µs.) at room temperature. The PL microscopy images were obtained from the TCS-SP8 X confocal microscope (Leica, Germany) with the excitation wavelength of 405 nm. Enantiomers of 3 were tried to resolve from a racemic mixture using HPLC with a CHIRALCEL OD column (10 mm × 250 mm) [a single-injection amount: 1 mg; tR = 14.52 min and 15.56 min (flow rate: 1.0 mL min<sup>-1</sup>; solvent: nHexane/iPrOH = 99.5/0.05, v/v)]. The electrical conductivity of **1** in crystal at room temperature was measured on a SZT-2A Four-Point Probe Meter.

*In-situ* high-pressure absorption, PL and Raman experiments were performed at ambient temperature by a diamond anvil cell (DAC). A piece of crystal was placed in the hole (diameter: 150 µm) of a T301 steel gasket with silicone oil as a pressure transmitting medium (PTM). The slope ( $\eta$ , piezochromic sensitivity) of the PL peak-external pressure plot was calculated by the equation ( $\eta = (\lambda_1 - \lambda_2)/(P_1 - P_2)$ ), where  $\lambda_1$  and  $\lambda_2$  refer to the PL peaks at pressures of  $P_1$  and  $P_2$ . A 355 nm line of a UV DPSS laser with the power of 5.0 mW, was used for PL measurements. The high-pressure evolution of steady-state PL spectra was collected by a modified spectrophotometer (Ocean Optics, QE65000). The laser beam passed through tunable filter and was focused onto the sample with a spot size of 20 mm. Each new acquisition was carried out several minutes later after elevation of the pressure, aiming to restrain any kinetic factor during the measurements. In situ Raman spectra were obtained at high pressure in the standard backscattering geometry with the Acton SpectraPro 2500 spectrometer. In situ UV-vis absorption spectra were measured on an Ocean Optics QE65000 spectrophotometer.

Device fabrication and measurement.

In a general procedure, ITO-coated glass substrate was etched, patterned, and washed with detergent, deionized water, Two and ethanol in turn. multilayer electroluminescence devices indium-tin oxide acetone, (ITO)/1,4,5,8,9,11-hexaazatriphenylenehexacarbonitrile (HATCN, 10 nm)/N,N'-bis(I)naphthyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB, 100 nm)/tris(4-carbazoyl-9-ylphenyl)amine (TCTA, 0 nm (OLED-1) and 10 nm (OLED-1'))/1(20 nm)/1,3,5-tri(phenyl-2-benzimidazole)benzene (TPBi, 60 nm)/Liq(2 nm)/Al(100 nm) were fabricated by the vapor deposition processes (1 served as the emitter layer, HATCN worked as the hole injection layer, TCTA was the hole transporting layer, and TPBi functioned as the electron-transporting material.). Organic layers were deposited by high-vacuum ( $\approx 4 \times 10^{-4}$  Pa) thermal evaporation with a rate of 0.1~0.2 nm s<sup>-1</sup>. The layer thickness and the deposition rate were monitored in situ by an oscillating guartz thickness monitor. The devices without encapsulation were measured immediately after fabrication under ambient atmosphere at room temperature. Electroluminescent (EL) spectra of the devices were measured by a PR655 spectroscan spectrometer. The luminance-voltage and currentevoltage characteristics were recorded using an optical power meter and a Keithley 2400 voltage current source. Device OLED-1 turned on at a voltage of 5.0 V, whilst device OLED-1' turned on at the lower voltage of 3.8 V.

### Syntheses.

Compound 1. The compound was synthesized according to the literature.<sup>3</sup> The single crystals for all the tests were obtained by the slow evaporation method in EA/PE.<sup>3</sup> <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>, 400 MHz): 8.31 (d, *J* = 8 Hz, 4H), 7.58-7.54 (m, 4H), 6.92 (d, *J* = 8 Hz, 2H), 6.81-6.79 (m, 2H). MP (°C) of single crystals 1: 171~172.

Compound **2**. **1** (320 mg, 1.0 mmol) and CuBr<sub>2</sub> (44.6 mg, 0.2 mmol) were mixed in 20 mL acetonitrile, and then subsequently stirred at 40 °C under N<sub>2</sub> atmosphere in 5 h. After the reaction mixture was filtered and evaporated, the raw product was purified by column chromatography (EA/PE, 1:1.5). The orange-red product was obtained with a yield of 42%. The single crystal of **2** was prepared by the slow evaporation method in acetonitrile. <sup>1</sup>H-NMR (600 MHz, DMSO):  $\delta$  9.43 (s, 1H), 9.35 (s, 1H), 8.97 (s, 1H), 8.36 (s, 1H), 7.81 (s, 1H), 7.68 (s, 1H), 7.52 (s, 1H), 7.40 (s, 1H), 7.14 (s, 1H), 6.91 (s, 1H). <sup>13</sup>C NMR (151 MHz, DMSO):  $\delta$  156.05, 150.21, 148.55, 147.61, 146.90, 137.83, 130.71, 128.41, 128.14, 128.09, 126.44, 118.26, 115.89, 112.88, 112.77, 99.59. EI-MS (M+H)<sup>+</sup>: 319.32. Elemental analysis calcd. (%) for C<sub>16</sub>H<sub>10</sub>N<sub>6</sub>S: C 60.36, H 3.17,N 26.40, S 10.07; found: C 60.40, H 3.21, N 26.43, S 10.11. MP (°C) of single crystals **2**: 165~167.

Compound **3**. 1 (320 mg, 1.0 mmol) and Cu(NO<sub>3</sub>)<sub>2</sub>•3H<sub>2</sub>O (56.78 mg, 0.2 mmol) were added into 10 mL mixed solvent ( $V_{\text{acetonitrile}}$  :  $V_{\text{DMF}} = 2$  : 3), and then heated at 100 °C for 20 h in a Schlenk tube. When the reaction mixture was slowly cooled down to room temperature, the yellow microcrystal of product were precipitated. The yield was of 88%. The crystal

of **3** for single-crystal X-ray diffraction test was prepared by the slow evaporation method in the reaction mixture. On the other hand, compound **3** could be prepared by the further conversion of **2** in the same reaction condition with the shorted reaction time (16 h). <sup>1</sup>H-NMR (600 MHz, DMSO)  $\delta$  9.33 (d, 2H), 7.96 (d, 2H), 7.61 (t, 3H), 7.27 (t, 3H). Elemental analysis calcd. (%) for C<sub>16</sub>H<sub>8</sub>N<sub>6</sub>S: C 60.75, H 2.55, N 26.57, S 10.14; found: C 60.72, H 2.51, N 26.53, S 10.16. MP (°C) of single crystals **3**: 173~175.

### Crystal Data Collection and Refinement.

Crystal Data Collection and Refinement. Crystal structure of compound **2** and **3** determination by X-ray diffraction was performed on a Rigaku Saturn 724 CCD area detector with a graphite monochromator for the X-ray source (Mo-K $\alpha$ radiation,  $\lambda = 0.710$  73 Å) operating at 50 kV and 40 mA. The data were collected by multi-scan mode at 293(2) K; the crystal-to-detector distance was 40 mm. Crystal structure of compound **2** and **3** determination by X-ray diffraction was performed on Bruker D8 VENTURE with the X-ray source (Mo-K $\alpha$  radiation,  $\lambda = 0.710$  73 Å) at temperature of 295 K. The structures were solved by direct methods and refined by full-matrix least-squares and difference Fourier techniques, based on  $F^2$ , using ShelXL. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were positioned geometrically and refined using a riding model. All the hydrogen atoms were included in the final refinement. The final formulas were determined by combing element analyses, and TGA. Crystallographic data for **2** and **3** have been deposited at the Cambridge Crystallographic Data Centre with CCDC reference numbers 1445532 and 1449464.

Compound	2	3
Formula	C16 H10 N6 S	C16 H8 N6 S
Formula weight	318.36	316.34
Crystal system	Monoclinic	Monoclinic
Space group	P 21/c	C 2/c
a (Å)	4.3851 (9)	7.5970(12)
b (Å)	14.235(3)	10.4069(14)
c (Å)	22.086(4)	16.527(2)
α(°)	90	90
β(°)	92.42(3)	96.452(6)°
γ(°)	90	90
$V(Å^3)$	1377.5(5)	1298.4(3)
Ζ	4	4
$D_c (g/cm^3)$	1.535	1.618
Abs coeff/mm <sup>-1</sup>	0.244	0.258
F(000)	656.0	648.0
$\theta$ range for data collection (°)	4.67 / 55.774	6.668 / 55.244
Data/restraints/parameters	3274/0/248	1506/0/105
GOF	1.400	1.051
$R\left[I > 2\sigma(I)\right]$	$R_1 = 0.1129$ $wR_2 = 0.1398$	$R_1 = 0.0437$ $wR_2 = 0.1025$
R (all data)	$R_1 = 0.1311$ $wR_2 = 0.1455$	$R_1 = 0.0642$ $wR_2 = 0.1124$

 Table S1. X-ray diffraction data collection and refinement parameters for 2 and 3.

2							
S(1)-N(2)	1.625(3)	N(2)-C(2)	1.340(4)	C(10)-C(9)	1.419(6)		
S(1)-N(1)	1.627(3)	N(1)-C(1)	1.342(4)	C(16)-C(15)	1.360(6)		
N(4)-C(5)	1.389(4)	C(5)-C(6)	1.388(5)	C(9)-C(8)	1.358(6)		
N(4)-C(7)	1.402(4)	C(5)-C(4)	1.419(5)	C(13)-C(14)	1.366(6)		
N(4)-C(11)	1.375(4)	C(6)-C(1)	1.422(5)	C(15)-C(14)	1.390(6)		
N(3)-C(6)	1.374(4)	C(3)-C(4)	1.367(5)	C(10)-C(9)	1.419(6)		
N(3)-C(7)	1.334(5)	C(3)-C(2)	1.444(5)				
N(5)-C(3)	1.396(5)	C(12)-C(13)	1.400(5)				
N(5)-C(12)	1.388(5)	C(7)-C(8)	1.407(5)				
N(6)-C(12)	1.330(4)	C(11)-C(10)	1.349(5)				
N(6)-C(16)	1.349(5)	C(2)-C(1)	1.443(5)				
		3					
S(1)-N(1)	1.6227(17)	N(1)-C(1)	1.340(2)	C(8)-C(7)	1.344(3)		
$S(1)-N(1^{1})$	1.6227(17)	C(4)-C(5)	1.414(3)	C(5)-C(6)	1.350(3)		
N(3)-C(4)	1.408(2)	$C(3)-C(3^1)$	1.430(3)	C(6)-C(7)	1.418(3)		
N(3)-C(3)	1.385(2)	C(3)-C(2)	1.399(2)				
N(3)-C(8)	1.382(2)	$C(1)-C(1^1)$	1.437(4)				
N(2)-C(4)	1.325(2)	N(1)-C(1)	1.340(2)				
N(2)-C(2)	1.365(2)	C(1)-C(2)	1.438(3)				

Table S2. Selected bond lengths  $(\text{\AA})$  for 2 and 3.

Table S3. Selected bond angles (°) for 2 and 3.

			2		
N(2)-S(1)-C(1)	100.87(17)	N(5)-C(3)-C(2)	116.2(3)	C(1)-C(2)-C(3)	123.2(3)
C(5)-N(4)-C(7)	106.5(3)	C(4)-C(3)-N(5)	126.0(3)	N(1)-C(1)-C(6)	128.4(4)
C(11)-N(4)-C(5)	131.1(3)	C(4)-C(3)-N(2)	117.8(3)	N(1)-C(1)-C(2)	113.8(3)
C(11)-N(4)-C(7)	122.4(3)	N(5)-C(12)-C(13)	117.7(3)	C(6)-C(1)-C(2)	117.8(3)
C(7)-N(3)-C(6)	103.9(3)	N(6)-C(12)-N(5)	119.2(3)	C(11)-C(10)-C(9)	120.2(4)
C(12)-N(5)-C(3)	128.2(3)	N(6)-C(12)-C(13)	123.2(4)	N(6)-C(6)-C(15)	125.0(4)
C(12)-N(6)-C(16)	116.2(4)	C(3)-C(4)-C(5)	118.1(3)	C(8)-C(9)-C(10)	121.0(4)
C(2)-N(2)-S(1)	106.5(3)	N(4)-C(7)-C(8)	117.8(3)	C(14)-C(13)-C(12)	118.5(4)
C(1)-N(1)-S(1)	105.9(3)	N(3)-C(7)-N(4)	112.3(3)	C(9)-C(8)-C(7)	119.5(4)
N(4)-C(5)-C(4)	128.6(3)	N(3)-C(7)-C(8)	129.9(4)	C(16)-C(15)-C(14)	117.6(4)
C(6)-C(5)-N(4)	104.5(3)	C(10)-C(11)-N(4)	119.1(4)	C(13)-C(14)-C(15)	119.5(4)
N(3)-C(6)-C(5)	112.8(3)	N(2)-C(2)-C(3)	123.9(3)		
N(3)-C(6)-C(1)	131.0(3)	N(2)-C(2)-C(1)	112.9(3)		
			3		
N(1)-S(1)-N(1 <sup>1</sup> )	101.09(12)	N(3)-C(3)-C(3 <sup>1</sup> )	135.15(9)	C(6)-C(5)-C(4)	119.40(17)
C(3)-N(3)-C(4)	106.29(14)	N(3)-C(3)-C(2)	104.43(14)	C(5)-C(6)-C(7)	120.44(18)
C(8)-N(3)-C(4)	120.86(15)	$C(2)-C(3)-C(3^1)$	120.42(10)	C(8)-C(7)-C(6)	121.12(19)
C(8)-N(3)-C(3)	132.57(15)	N(1)-C(1)-C(1 <sup>1</sup> )	113.52(11)		
C(4)-N(2)-C(2)	104.67(15)	N(1)-C(1)-C(2)	126.98(17)		
C(1)-N(1)-S(1)	105.93(14)	C(1 <sup>1</sup> )-C(1)-C(2)	119.48(10)		
N(3)-C(4)-C(5)	118.51(16)	N(2)-C(2)-C(3)	112.43(16)		
N(2)-C(4)-N(3)	112.07(15)	C(3)-C(2)-C(1)	119.79(16)		
N(2)-C(4)-C(5)	129.42(16)	C(7)-C(8)-N(3)	119.14(17)		



Figure S1. The crystal structure of compound 3.



Figure S2. The attempt to resolve into the *M* and *P* enantiomers of compound 3 by chiral HPLC.

## Computational details for monomeric 1-3.

Density functional theory  $(DFT)^{4, 5}$  has been applied to the determination of the ground-state geometry of the isolated molecule, and its lowest-lying singlet excited states have been characterized within time-dependent DFT  $(TDDFT)^{6-8}$ . All calculations have been performed with the Gaussian 09 program package.<sup>9</sup> The geometry optimization was carried out with the B3LYP<sup>10, 11</sup> functional using 6-311++G(2df, 2pd) basis set, and the TDDFT electronic excitation calculations were performed at the same level. The solvent (DCM) effect of dichloromethane was taken into account for all calculations by the self-consistent reaction field (SCRF) method, which is based on the integral equation formalism variant (IEFPCM).<sup>12</sup>





# Cartesian coordinates of the studied models:

2

S	-0.148392000000	4.180078000000	0.000012000000
Ν	-1.513954000000	3.296272000000	-0.000018000000
Ν	0.957980000000	2.979802000000	0.000053000000
Ν	-3.326820000000	0.710531000000	-0.000006000000
Ν	-2.316540000000	-1.318833000000	-0.000107000000
Ν	2.296580000000	0.558031000000	0.000015000000
Н	2.671928000000	1.494218000000	-0.000007000000
Ν	2.811463000000	-1.730295000000	0.000169000000
С	-1.151902000000	2.017324000000	-0.000020000000
С	0.282540000000	1.833568000000	0.000021000000
С	0.909694000000	0.530586000000	0.000025000000
С	0.096493000000	-0.576192000000	-0.000053000000
Н	0.536338000000	-1.558306000000	0.000014000000
С	-1.306191000000	-0.379201000000	-0.000047000000
С	-1.974124000000	0.851782000000	-0.000036000000

С	3.224829000000	-0.462181000000	0.000047000000	
С	4.592349000000	-0.117154000000	-0.000061000000	
Н	4.892348000000	0.922336000000	-0.000129000000	
С	5.527893000000	-1.126453000000	-0.000122000000	
Н	6.582534000000	-0.885790000000	-0.000223000000	
С	5.101856000000	-2.456827000000	-0.000018000000	
Н	5.804821000000	-3.276617000000	-0.000179000000	
С	3.740160000000	-2.693376000000	0.000171000000	
Н	3.360448000000	-3.708802000000	0.000224000000	
С	-2.279422000000	-2.688161000000	-0.000149000000	
Н	-1.303686000000	-3.148144000000	-0.000267000000	
С	-3.445774000000	-3.384675000000	-0.000033000000	
Н	-3.412381000000	-4.463475000000	0.000004000000	
С	-4.691859000000	-2.698822000000	0.000077000000	
Н	-5.609722000000	-3.269271000000	0.000202000000	
С	-4.735134000000	-1.333003000000	0.000067000000	
Н	-5.664623000000	-0.783860000000	0.000117000000	
С	-3.532189000000	-0.595897000000	0.000013000000	
3				
S	-4.462311000000	-0.000006000000	-0.000002000000	
Ν	1.233609000000	1.697948000000	0.033796000000	
Ν	-0.752176000000	2.760068000000	-0.235582000000	
Ν	-3.414576000000	1.236966000000	-0.176505000000	
С	0.551069000000	2.930945000000	-0.127468000000	
С	0.261956000000	0.713195000000	-0.031165000000	
С	-2.196955000000	0.715041000000	-0.101916000000	
С	-0.948178000000	1.421687000000	-0.154235000000	
С	2.574127000000	1.676904000000	0.339316000000	
Н	3.005203000000	0.728893000000	0.604378000000	
С	1.304076000000	4.122850000000	-0.128336000000	
Н	0.771974000000	5.048359000000	-0.288648000000	
С	2.650369000000	4.077893000000	0.094319000000	
Н	3.233288000000	4.987433000000	0.103619000000	
С	3.284353000000	2.834895000000	0.357256000000	
Н	4.334881000000	2.794018000000	0.602125000000	
Ν	1.233614000000	-1.697945000000	-0.033795000000	
Ν	-0.752167000000	-2.76007000000	0.235588000000	
Ν	-3.414573000000	-1.236976000000	0.176503000000	
С	0.551078000000	-2.930943000000	0.127475000000	
С	0.261958000000	-0.713194000000	0.031163000000	
С	-2.196953000000	-0.715047000000	0.101914000000	
С	-0.948174000000	-1.421690000000	0.154235000000	
С	2.574130000000	-1.676897000000	-0.339323000000	
Η	3.005201000000	-0.728886000000	-0.604393000000	
С	1.304089000000	-4.122846000000	0.128344000000	
Η	0.771991000000	-5.048355000000	0.288661000000	
С	2.650381000000	-4.077885000000	-0.094317000000	

Н	3.233303000000	-4.987423000000	-0.103615000000
С	3.284360000000	-2.834886000000	-0.357261000000
Н	4.334887000000	-2.794007000000	-0.602135000000



Figure S4. Energies and topologies (isosurface value 0.020) of  $\pi$ - and  $\pi$ \*-type MOs for compound 2.



Figure S5. Energies and topologies (isosurface value 0.020) of  $\pi$ - and  $\pi$ \*-type MOs for compound 3.



**Figure S6**. Electronic absorption spectrum of **1** in a DCM solution, together with the calculated  $S_0 \rightarrow S_n$  transitions at the TD-B3LYP level of theory. Inset: DFT-optimized structure of **1** in the electronic ground state (S<sub>0</sub>) and the TD-DFT calculated  $S_0 \rightarrow S_1$  transition dipole moment (blue line with arrow displaying the orientation of transition dipole moment ).



**Figure S7**. Electronic absorption spectrum of **2** in a DCM solution, together with the calculated  $S_0 \rightarrow S_n$  transitions at the TD-B3LYP level of theory. Inset: DFT-optimized structure of **2** in the electronic ground state (S<sub>0</sub>) and the TD-DFT calculated  $S_0 \rightarrow S_1$  transition dipole moment (blue line with arrow displaying the orientation of transition dipole moment ).



**Figure S8**. Electronic absorption spectrum of **3** in a DCM solution, together with the calculated  $S_0 \rightarrow S_n$  transitions at the TD-B3LYP level of theory. Inset: DFT-optimized structure of **3** in the electronic ground state (S<sub>0</sub>) and the TD-DFT calculated  $S_0 \rightarrow S_1$  transition dipole moment (blue line with arrow displaying the orientation of transition dipole moment ).

Table S4. Values of energies, wavelength, oscillator strengths and dominant contributions of the respective molecular orbitals for  $S_0 \rightarrow S_n$  of 1.

State	Energy (eV)	Wavelength (nm)	Oscillator strength	Major MO $\rightarrow$ MO contributions (%)
$\mathbf{S}_1$	2.09	595.0	0.1597	HOMO $\rightarrow$ LUMO (99)
$S_2$	3.42	363.5	0.0280	H-1→LUMO (99)
<b>S</b> <sub>3</sub>	3.63	342.5	0.1702	HOMO→L+1 (94)
$S_4$	3.69	336.5	0.0601	HOMO→L+2 (94)
$S_5$	3.98	312.5	0.7336	HOMO→L+3 (98)
$S_6$	4.19	296.5	0.1068	HOMO→L+4 (52) H-4→LUMO (33)
$S_7$	4.24	293.0	0.0013	H-3→LUMO (58) H-2→LUMO (40)
$S_8$	4.24	293.0	0.0053	H-2→LUMO (56) H-3→LUMO (41)
<b>S</b> <sub>9</sub>	4.34	286.5	0.0019	HOMO→L+5 (98)
S <sub>10</sub>	4.42	281.0	0.0062	HOMO→L+6 (86)

Table S5. Values of energies, oscillator strengths and dominant contributions of the respective molecular orbitals for  $S_0 \rightarrow S_n$  of 2.

State	Energy (eV)	Wavelength (nm)	Oscillator strength	Major MO $\rightarrow$ MO contributions (%)
$S_1$	2.46	505.5	0.0879	HOMO $\rightarrow$ LUMO (99)
$S_2$	3.30	376.5	0.1651	HOMO→L+1 (94)
S <sub>3</sub>	3.68	337.5	0.1223	H-1→LUMO (92)
$S_4$	3.89	319.5	0.0744	HOMO→L+2 (97)
$S_5$	4.02	309.0	0.2115	H-2→LUMO (89)
$S_6$	4.28	290.5	0.1410	HOMO $\rightarrow$ L+3 (73) H-1 $\rightarrow$ L+1(16) H-2 $\rightarrow$ L+1 (6)
$S_7$	4.42	281.0	0.0833	H-3→LUMO (89)
$S_8$	4.47	278.0	0.4411	$\begin{array}{c} \text{H-1} \rightarrow \text{L+1(69)} \\ \text{HOMO} \rightarrow \text{L+3}  (20) \end{array}$
S9	4.64	268.0	0.0072	HOMO $\rightarrow$ L+4 (44) H-2 $\rightarrow$ L+1 (30) H-4 $\rightarrow$ LUMO (12) H-1 $\rightarrow$ L+1(9)
S <sub>10</sub>	4.65	267.5	0.0682	H-4 $\rightarrow$ LUMO (44) HOMO $\rightarrow$ L+5 (28) HOMO $\rightarrow$ L+4 (15)

Table S6. Values of energies, oscillator strengths and dominant contributions of the respective molecular orbitals for  $S_0 \rightarrow S_n$  of 3.

State	Energy (eV)	Wavelength (nm)	Oscillator strength	Major MO $\rightarrow$ MO contributions (%)
$S_1$	2.73	454.5	0.032	HOMO $\rightarrow$ LUMO (99)
$S_2$	3.39	366.0	0.0808	HOMO→L+1 (93)
<b>S</b> <sub>3</sub>	3.47	358.0	0.1601	HOMO→L+2 (97)
$S_4$	3.88	320.5	0.4162	H-1→LUMO (93)
<b>S</b> <sub>5</sub>	4.22	294.5	0.0127	HOMO→L+3 (46) H-1→L+1(39) H-2→LUMO (13)
$S_6$	4.31	288.0	0.0208	H-2→LUMO (85) H-1→L+1(8)
$S_7$	4.33	287.0	0.0496	H-3→LUMO (60) H-1→L+2(36)
S <sub>8</sub>	4.51	275.5	0.5947	H-1 $\rightarrow$ L+1(50) HOMO $\rightarrow$ L+3 (41) H-3 $\rightarrow$ L+2(6)
<b>S</b> <sub>9</sub>	4.53	274.5	0.2348	H-1→L+2 (56) H-3→LUMO (34)
S <sub>10</sub>	4.77	260.5	0.0003	HOMO→L+4 (92)

**Table S7.** Absorption maximum  $A_{\text{max}}$ , and emission maximum  $E_{\text{max}}$ , and Stokes shift  $v_{\text{ST}}$  of 1 and 2 in various solvents ( $\Delta f$  refers to the solvent polarity parameter).

Solvent		AE	$A_{\max}$ [cm <sup>-1</sup> ]		$E_{\max} [\mathrm{cm}^{-1}]$		$v_{\rm ST}[\rm cm^{-1}]$		
	ε	n	$\Delta J$	1	2	1	2	1	2
МеОН	32.6	1.3290	0.309	21050	22120	16980	17270	4070	4850
Acetonitrile	37.5	1.3440	0.305	20575	21835	16000	16750	4575	5085
EtOH	24.3	1.3600	0.288	20700	22000	17015	17420	3685	4580
DMF	36.7	1.4290	0.279	19960	21435	15780	16665	4180	4770
DCM	9.1	1.4240	0.219	20200	21690	16285	17095	3915	4595
n-hexane	1.9	1.3750	-0.007	19800	21975	16475	18330	3325	3645

Table S4 summarizes the related spectroscopic data. The solvent polarity parameter  $\Delta f$  is calculated from

Equation (1), where  $\varepsilon$  and *n* are the dielectric constant and the refractive index of the solvent, respectively.

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

The different Stokes shifts ( $v_{ST}$ ) can be plotted as a function of solvent polarity parameters ( $\Delta f$ ). Generally,  $v_{ST} vs \Delta f$  correlation allows to quantify the difference in polarization between ground state and excited state of the molecule. The Lippert-Mataga model for dipolar D-A systems, in general one estimates from this correlation the difference of electric dipole moments between excited state and ground state according to Equation (2);  $\mu_e$  and  $\mu_g$  are the electric dipole moments of excited state and ground state, respectively, *h* is Planck's constant, and *c* is the velocity of light and *a* is the Onsager radius which is the radius of a spherical cavity containing the dipole. Hence, it is of 9.1 Debye for compound 1, and it is of 6.9 Debye for compound 2.

$$v_{ST} = \frac{2 \cdot \left(\mu_e - \mu_g\right)}{h \cdot c \cdot a^3} \cdot \Delta f + C = 10070 \cdot \frac{\left(\mu_e - \mu_g\right)}{a^3} \cdot \Delta f + C$$
(2)



**Figure S9**. UV/Vis absorption (a) and fluorescence (b) spectra of compound 1 in different solvents. (c)  $v_{ST} vs \Delta f$  plots for 1 at room temperature. (\* Instrumental error).



**Figure S10**. UV/Vis absorption (a) and fluorescence (b) spectra of compound **2** in different solvents. (c)  $v_{ST} vs \Delta f$  plots for **2** at room temperature. (\* Instrumental error).



Figure S11. (a-c) Excitation and PL spectra of 1-3 in PMMA film.

**Table S8**. Selected absorption and emission peaks, fluorescence lifetimes  $\tau_r$ , quantum yields  $\Phi_r$  of 1-3, and rate constants for radiative  $k_r$  and nonradiative deactivation  $k_{nr}$ , extracted via  $\Phi_r = k_r \cdot \tau_r = k_r / (k_r + k_{nr})$ .

	System	$\lambda_{\rm max}({\rm abs})/{\rm nm}$	$\lambda_{\rm max}({\rm em})/{\rm nm}$	$\Phi_{ m r}$ /%	$\tau_r/ns$	$K_{\rm r}/{\rm ns}^{-1}$	$k_{\rm nr}/{\rm ns}^{-1}$
1	PMMA film	431	540	12.5 <sup>c</sup>	13.20	0.01	0.07
2	PMMA film	420	490	$2.9^{c}$	12.63	0.002	0.08
3	PMMA film	394	465	$0.8^{c}$	10.89	0.0007	0.09



**Figure S12.** UV-vis absorption and PL spectra for the single crystals of **1-3** (a-c). Inset: The photographs for the single crystals of **1-3** under UV light.



Figure S13. The packing diagram of compound 1 with an emphasis on  $\pi$ - $\pi$  interaction (magenta).



Figure S14. The packing diagram of compound 3 with an emphasis on  $\pi$ - $\pi$  interaction (magenta).



Figure S15. The packing diagram of compound 2 with an emphasis on  $\pi$ - $\pi$  interaction (magenta).



**Figure S16**. UV/Vis absorption spectra of compound **1** (a) and **2** (b) in DMF with different concentrations. (Black:  $5 \times 10^{-6}$  M; red:  $1 \times 10^{-5}$  M; green:  $5 \times 10^{-5}$  M; blue:  $1 \times 10^{-4}$  M; cyan:  $5 \times 10^{-4}$  M; magenta:  $1 \times 10^{-3}$  M. In  $5 \times 10^{-4}$  M or  $1 \times 10^{-3}$  M solution, 5 mm quartz cell was used. In the other solutions, 1 cm quartz cell was used.)



Figure S17. UV/Vis absorption (a) and PL (b) spectra of compound 1 in DMF and mixed solvents  $H_2O/DMF$  (v / v = 20 : 80; 50 : 50; 80 : 20; 96 : 6; 97 : 3; 98 : 2; 99 : 1). (\* Instrumental error)



Figure S18. Powder X-ray diffraction data of compound 1 obtained by different ways. 1-Sediment: after adding water into the DMF solution of 1 ( $f_w = 99\%$ ), such mixture was put in the dark without any interference at room temperature in 10 h; and then the sediment was obtained and collected at the bottom of solution



Figure S19. UV-vis absorption and PL spectra of compound 1 in solid states obtained by different ways. (1-crystal: The single crystals of 1 was obtained by the slow evaporation in EA/PE. 1-Sediment: after adding water into the DMF solution of 1 ( $f_w = 99\%$ ), such mixture was put in the dark without any interference at room temperature in 10 h; and then the sediment was collected at the bottom of solution.)



Figure S20. UV-vis absorption (a) and PL (b) spectra for samples I, II and the upper solution of III of compound 1.



Figure S21. UV/Vis absorption (a) and PL (b) spectra of 2 in DMF and mixed solvents  $H_2O/DMF$  (v / v = 20 : 80; 50 : 50; 80 : 20; 96 : 6; 97 : 3; 98 : 2; 99 : 1). (\* Instrumental error)



**Figure S22**. The photographs of **2** in DMF (I), immediately in the mixed solvent  $H_2O/DMF$  (II, v / v = 99 : 1) and in the mixed solvent  $H_2O/DMF(v / v = 99 : 1)$  for 10 h (III) under natural light (a) and the UV light of 365 nm (b), respectively. UV/Vis absorption (c) and PL (d) spectra of samples I, II and the upper solution of III.



Figure S23. Powder X-ray diffraction data of 2 obtained by different ways.



Figure S24. UV-vis absorption and PL spectra of 2 in solid states obtained by different ways. (2-crystal: The single rystals of 2. 2-Sediment: after adding water into the DMF solution of 2 ( $f_w = 99\%$ ), such mixture was put in the dark without any interference at room temperature in 10 h; and then the sediment was collected at the bottom of solution.



Figure S25. In-situ UV-vis absorption (a) and PL (b) spectra of 1 in crystal under decompression process.



**Figure S26**. (a) In-situ UV-vis absorption spectra of **2** in crystal under decompression process. (b) The steady-state PL spectra of **2** in crystal at 1 atm and after decompression at 1 atm.



Figure S27. In-situ UV-vis absorption (a) and PL (b) spectra of 3 in crystal under decompression process.



Figure S28. The changes in the absorption at the excitation wavelength (355 nm) of 1-3 in crystal under pressure.



Figure S29. The corresponding plots of the relative hydrostatic pressure versus fluorescence peaks for single crystals 1 (a), 2 (b) and 3 (c).



**Figure S30**. The *In-situ* Raman spectra of single crystals **1** (a), **2** (b) and **3** (c) under different hydrostatic pressures (GPa). (Peaks 1-5 were belonged to the pyridine unit, and peaks 6-9 were belonged to the BTD unit.)



Figure S31. Thermogravimetric analysis result of 1 in crystal.



**Figure S32**. (a) CIE coordinates for PL of **1** in crystal (PL-**1**), devices OLED-**1** (ITO/HATCN(10 nm)/NPB(150 nm)/1(20 nm)/TPBi(60 nm)/Liq (2 nm)/Al) and OLED-**1**' (ITO/HATCN(10 nm)/NPB(100 nm)/TCTA(10 nm)/1(20 nm)/TPBi(60 nm)/Liq(2 nm)/Al); inset: the photographs of **1** in crystal under 365 nm UV light and device OLED-**1**'. (b) The performances of PL of **1** in crystal and EL of devices OLED-**1** and OLED-**1**'.



Figure S33. EL spectra of device OLED-1 upon increasing the driving bias voltages.



Figure S34. EL spectra of device OLED-1' upon increasing the driving bias voltages.

### Computational models and methods for the dimmer of 1

The computational models for dimmers of **1** were constructed to mimic its neutral, cationic, or anionic microenvironment created by a neighbouring molecule in various ionic states. The dimmer structure was extracted from the measured crystal structure. The emission spectra of these three models were simulated by investigating their  $S_1 \rightarrow S_0$  vertical electronic transition energies, by applying a Frozen Density Embedding Theory (FDET)<sup>13</sup> based method within the linear-response time-dependent density functional theory (TDDFT)<sup>14</sup> framework. The FDET combined with TDDFT is a state-of-the-art method to explore the effect of explicit environment in a fully quantum-mechanical level on the electronic properties of molecules, which has been widely used to investigate the quantum-mechanical effect of solvent, solid, and protein environment on molecular electronic properties.<sup>15</sup> This method partitions the entire system as two regions – the target system (embedded system) and its environment.

In this work, one molecule in the dimmers was stimulated to excited state, but the other one was at its ground state. Their packing structure was identical to the previously rearranged structure at neutral, cationic, or anionic states. The embedded system was treated with the B3LYP functional<sup>16</sup> and Slater-type orbitals (STO) DZP<sup>17</sup> basis sets. The frozen density of the environment was generated by a Kohn–Sham calculation<sup>18</sup> for the isolated environment at the B3LYP/STO-DZP level. The electron density of the embedded system and the charge density of the embedding environment uniquely determine the embedding potential within the FDET framework<sup>13</sup>. Its nonadditive exchange-correlation component was approximated using the local-density approximation<sup>18, 19</sup> and its nonadditive kinetic component was approximated by the NDSD<sup>20</sup> bifunctional. All calculations were performed within the ADF code (2017 version)<sup>21</sup>.

### Results

The calculated emission energies for compound 1 in a neutral, cationic, or anionic microenvironment are 493nm (2.52 eV), 525 nm (2.36 eV), or 504 nm (2.46 eV), respectively. This indicates the cationic microenvironment (possible EL environment) leads to a redshift of 0.16 eV in emission energy with respect to that in neutral environment (PL environment), which is very close to the measured redshift (0.14 eV). However, the anionic microenvironment results a significantly smaller redshift (0.06 eV) in emission energy. Therefore, the computational results indicate the cationic environment is the dominant EL environment of compound 1. (Note: The calculated shift in the emission energy is a relative energy, and its uncertainty (typically ~0.1 eV)<sup>8</sup> is much smaller than the uncertainty of the calculated absolute emission energy (~0.5 eV) that is due to the approximations applied in computational models and methods in this work.)

environment	neutral	cationic	anionic				
λ	493nm (2.52 eV)	525 nm (2.36 eV)	504 nm (2.46 eV)				

Table	<b>S9</b> .	Calculated	emission	energies	(λ)	of	compound	1	in	its	neutral,	cationic,	or	anionic
microe	nviro	nment.												

The Cartesian coordinates of the investigated dimer of compound 1.

С	2.70727	3.02133	2.19223
Н	2.89858	2.38224	2.84043
С	1.88688	4.04518	2.54247
Н	1.51553	4.09399	3.39391
С	1.62452	5.00946	1.59238
С	2.20035	4.90755	0.34038
С	3.00698	3.80931	0.07794
N	3.26327	2.86324	0.97772

Н	1.06336	5.72373	1.79364
Н	2.05253	5.55709	-0.30782
Ν	3.55627	3.68299	-1.19083
С	4.37766	2.70364	-1.72162
С	4.77484	1.52998	-1.11782
С	4.86851	2.93142	-3.03578
Н	4.47935	1.33690	-0.25750
С	5.62280	0.60901	-1.78476
С	5.75031	2.01309	-3.68595
Ν	4.58340	4.01217	-3.78066
Н	5.83480	-0.18410	-1.34770
С	6.14670	0.81406	-3.02690
Ν	6.11742	2.41980	-4.91525
Ν	7.01497	-0.09321	-3.67509
С	8.22896	-0.49721	-3.19659
Ν	8.85151	-1.41176	-3.95430
С	8.81735	0.01082	-2.03240
С	10.07395	-1.80353	-3.58137
Н	8.35900	0.61277	-1.49174
С	10.07554	-0.39725	-1.70880
Н	10.50104	-2.44657	-4.10032
С	10.73848	-1.32295	-2.48821
Н	10.49213	-0.04815	-0.95503
Н	11.59869	-1.60694	-2.28004
Н	3.35268	4.31619	-1.73543
Н	6.75894	-0.41563	-4.42984
S	5.39314	3.83202	-5.16496
Η	7.72942	3.14987	0.30782
С	5.40429	6.00332	1.72162
С	5.00711	7.17698	1.11782
Н	5.30260	7.37006	0.25750
С	4.15915	8.09795	1.78476
Н	3.94715	8.89106	1.34770
С	3.63525	7.89290	3.02690
С	4.03164	6.69387	3.68595
С	4.91344	5.77554	3.03578
Н	1.42295	8.09418	1.49174
Ν	6.22568	5.02396	1.19083
Н	6.42927	4.39076	1.73543
Ν	5.19855	4.69479	3.78066
Ν	3.66453	6.28716	4.91525
Ν	2.76698	8.80017	3.67509
Н	3.02301	9.12259	4.42984
S	4.38881	4.87494	5.16496
C	6.77497	4.89765	-0.07794
C	1.55299	9.20417	3.19659
Ν	6.51868	5.84372	-0.97772

С	7.58160	3.79941	-0.34038
С	0.96460	8.69613	2.03240
N	0.93044	10.11872	3.95430
С	7.07468	5.68562	-2.19223
С	8.15742	3.69750	-1.59238
С	-0.29358	9.10421	1.70880
С	-0.29200	10.51048	3.58137
С	7.89507	4.66177	-2.54247
Н	6.88337	6.32471	-2.84043
Н	8.71859	2.98323	-1.79364
С	-0.95653	10.02991	2.48821
Н	-0.71018	8.75511	0.95503
Н	-0.71908	11.15353	4.10032
Н	8.26642	4.61296	-3.39391
Н	-1.81674	10.31390	2.28004



Figure S35. PL microscopy images of crystals 1-3 excited at 405 nm.



**Figure S36.** <sup>1</sup>H-NMR spectrum of compound **2**.



Figure S37. <sup>13</sup>C-NMR spectrum of compound 2.



Figure S38. <sup>1</sup>H-NMR spectrum of compound 3.

## Reference

1. Demas, J. N.; Crosby, G. A. J. Phys. Chem. 1971, 75, 991.

2. Kato, S.; Matsumoto, T.; Shigeiwa, M.; Gorohmaru, H.; Maeda, S.; Ishi-i, T.; Mataka S. Chem. Eur. J., 2006, 12, 2303.

3. Han, X.; Gong, W.; Tong, Y.; Wei, D.; Wang, Y.; Ding, J.; Hou, H.; Song, Y. Dyes Pigments., 2017, 137, 135.

4. P. Hohenberg, W. Kohn, Phys. Rev. 1964, 136, B864-B871.

5. W. Kohn, L. J. Sham, Phys. Rev. 1965, 140, A1133-A1138.

6. M. E. Casida, Time-Dependent Density Functional Response Theory for Molecules. In *Recent Advances in Density Functional Methods*; Chong, D. P., Ed.; World Scientific: Singapore, 1995; Vol. 1.

Tunctional Methods, Choing, D. T., Ed., World Scientific. Singapore, 1995, Vol.

7. R. Bauernschmitt, R. Ahlrichs, Chem. Phys. Lett., 1996, 256, 454-464.

8. R. E. Stratmann, G. E. Scuseria, M. J. Frisch, J. Chem. Phys., 1998, 109, 8218-8224.

Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

10. C. T. Lee, Yang, W. T., Parr. R. G., Phys. Rev. B 1988, 37, 785-789;

11. A. D. Becke, J. Chem. Phys. 1993, 98, 5648-5652.

12. S. Miertuš, E. Scrocco, and J. Tomasi, "Electrostatic Interaction of a Solute with a Continuum. A Direct Utilization of ab initio Molecular Potentials for the Prevision of Solvent Effects," *Chem. Phys.*, **55** (1981) 117-29.

13. (a) Wesolowski, T. A.; Warshel, J. Phys. Chem. 1993, 97, 8050-8053. (b) Wesolowski, T. A. Phys. Rev. A 2008, 77,

012504. (c) Pernal, K.; Wesolowski, T. A. Int. J. Quantum Chem. 2009, 109, 520-2525.

14. Casida, M. E.; Wesolowski, T. A. Int. J. Quantum Chem. 2004, 96, 577-588.

15. (a) Wesolowski, T. A; Shedge S.; Zhou X.; Chemical Reviews, 115 (12): 5891-5928, 2015. (b) Zhou, X.; Sundholm, D.;

Wesołowski, T. A.; Kaila, V. R. J. Am. Chem. Soc. 2014, 136, 2723-2726. (c) Zhou, X.; Wesolowski, T. A.; Tabacchi, G.;

Fois, E.; Calzaferri, G.; Devaux, Phys. Chem. Chem. Phys. 2013, 15, 159-167. (d) Zhou, X.; Kaminski, J. W.; Wesolowski,

T. A. Phys. Chem. Chem. Phys. 2011, 13, 10565–10576. (e) Artiukhin, D. G.; Neugebauer, J.; *The Journal of chemical physics*, 148(21), 214104, 2018.

16. (a) Becke, A. D. J. Chem. Phys. 1993, 98, 5648. (b) Lee, C. T.; Yang, W. T.; Parr, R. G. Phys. Rev. B 1988, 37, 785.

17. van Lenthe, E.; Baerends, E. J. J. Comput. Chem. 2003, 24, 1142.

18. Kohn, W.; Sham, L. J. Phys. Rev. 1965, 140, A1133.

19. Hohenberg, P.; Kohn, W. Phys. Rev. 1964, 136, B864.

21. E. J. Baerends, T. Ziegler, A. J. Atkins, J. Autschbach, D. Bashford, O. Baseggio, A. Bérces, F. M. Bickelhaupt, C. Bo, P. M. Boerritger, L. Cavallo, C. Daul, D. P. Chong, D. V. Chulhai, L. Deng, R. M. Dickson, J. M. Dieterich, D. E. Ellis, M. van Faassen, A. Ghysels, A. Giammona, S. J. A. van Gisbergen, A. Goez, A. W. Götz, S. Gusarov, F. E. Harris, P. van den Hoek, Z. Hu, C. R. Jacob, H. Jacobsen, L. Jensen, L. Joubert, J. W. Kaminski, G. van Kessel, C. König, F. Kootstra, A. Kovalenko, M. Krykunov, E. van Lenthe, D. A. McCormack, A. Michalak, M. Mitoraj, S. M. Morton, J. Neugebauer, V. P. Nicu, L. Noodleman, V. P. Osinga, S. Patchkovskii, M. Pavanello, C. A. Peeples, P. H. T. Philipsen, D. Post, C. C. Pye, H. Ramanantoanina, P. Ramos, W. Ravenek, J. I. Rodríguez, P. Ros, R. Rüger, P. R. T. Schipper, D. Schlüns, H. van Schoot, G. Schreckenbach, J. S. Seldenthuis, M. Seth, J. G. Snijders, M. Solà, S. M., M. Swart, D. Swerhone, G. te Velde, V. Tognetti, P. Vernooijs, L. Versluis, L. Visscher, O. Visser, F. Wang, T. A. Wesolowski, E. M. van Wezenbeek, G. Wiesenekker, S. K. Wolff, T. K. Woo, and A. L. Yakovlev, "ADF2017, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, https://www.scm.com."