

## Supporting information

### 4–Diphenylamino–phenyl substituted pyrazine: nonlinear optical switching by protonation

Liang Xu,<sup>†a</sup> Hai Zhu,<sup>†b</sup> Guankui Long,<sup>a</sup> Jun Zhao,<sup>c</sup> Dongsheng Li,<sup>c</sup> Rakesh Ganguly,<sup>d</sup> Yongxin Li,<sup>d</sup> Qing-Hua Xu<sup>\*b</sup> and Qichun Zhang<sup>\*a,d</sup>

<sup>a</sup>School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore. Email: qczhang@ntu.edu.sg.

<sup>b</sup>Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore. Email: chmxqh@nus.edu.sg

<sup>c</sup>College of Materials and Chemical Engineering, Hubei Provincial Collaborative Innovation Center for New Energy Microgrid, China Three Gorges University, Yichang 443002, P.R. China

<sup>d</sup>Division of Chemistry and Biological Chemistry, School of Physical and Mathematic Sciences, Nanyang Technological University, Singapore 637371, Singapore.

#### S1. Experimental

##### *S1.1 Reagents and instruments*

Most reagents were purchased from Alfa Aesar or Aldrich and used as supplied unless otherwise noted. All the solvents used in photophysical measurements and electrochemical measurements were of HPLC grade quality. All other solvents were obtained commercially and purified using standard procedures. Silica gel with 200-300 mesh were used in column chromatography, and precoated silica gel plates were utilized in thin-layer chromatography (TLC) and monitored by UV light. SHIMADZU GCMS-QP2010 puls spectrometer was employed in EI mass spectrometric measurements. Bruker Biflex III mass spectrometer was engaged in Matrix-assisted laser desorption/ionization reflectron time-of-flight (MALDI-TOF) mass spectrometry. Nuclear magnetic resonance (NMR) spectra were measured on Bruker Avance DPS-400 spectrometer at room temperature (298 K), and chemical shifts were referenced to the residual solvent peaks. Elemental analyses were recorded on a Carlo-Erba-1106 instrument. UV-Vis spectra were performed on a Hitachi U-3010 spectrometer, and Fluorescence emission spectra were monitored using a Hitachi F-4500.

Cyclic voltammetry measurements were monitored on a CHI660D electrochemical workstation (CH Instruments, Austin, TX). A dry weighing bottle was served as the container. The working electrode glassy

carbon (3.0 mm in diameter) was polished on a felt pad with 0.05 $\mu$ m alumina (Buehler, Ltd., Lake Bluff, IL), sonicated in deionized water for 2 min, and then dried before usage. The counter electrode platinum wire was rubbed with an abrasive paper, washed with deionized water and acetone, and dried. The reference electrode was platinum wires. Fc<sup>+</sup>/Fc was used as an internal standard. Potentials were recorded versus Fc<sup>+</sup>/Fc in a solution of anhydrous dichloromethane (DCM) with 0.1M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as a supporting electrolyte at a scan rate of 50 mV s<sup>-1</sup>.

### ***SI.2 Synthesis procedures and characterization data for new compounds***

#### **Synthesis of compound 2,3-bis(4-diphenylamino-phenyl) quinoxaline (**1**)**

1,2-Diaminobenzene (108 mg, 1.0 mmol) and 4,4'-bis(N,N-diphenylamino)benzil (540 mg, 1.0 mmol) were dissolved in anhydrous acetic acid (50 mL) with catalytic amount of 2-iodoxybenzoic acid (IBX). The solution was refluxed for 24 hours under Argon atmosphere. After that the crude product was concentrated in vacuo and purified by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether 1:2), affording compound **1** (554 mg, yield 90%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.15-8.13 (m, 2 H), 7.74-7.72 (m, 2 H), 7.44 (d,  $J$  = 9.0 Hz, 4 H), 7.29-7.25 (m, 8 H), 7.13 (d,  $J$  = 6.0 Hz, 8 H), 7.08-7.03 (m, 8 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  153.31, 148.71, 147.44, 141.13, 132.55, 130.94, 129.75, 129.50, 129.10, 125.13, 123.61, 122.29. HRMS (M+1) = 617.2708 (calc. 617.2705).

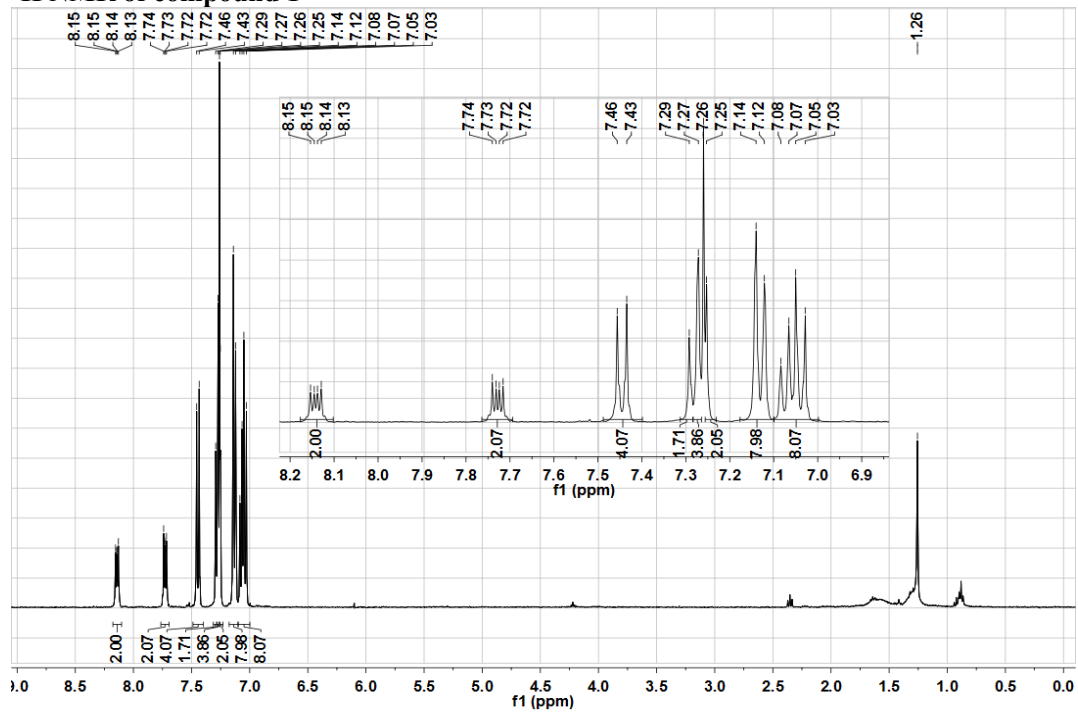
#### **Synthesis of compound 2,3-bis(4-diphenylamino-phenyl)-6,7-dimethylquinoxaline (**2**)**

The procedure was the same with above except that 1,2-Diaminobenzene was replaced by 4,5-Dimethyl-1,2-phenylenediamine (136 mg, 1.0 mmol). This reaction gave compound **2** (592 mg, yield 92%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.89 (s, 2 H), 7.42 (d,  $J$  = 6.0 Hz, 4 H), 7.28-7.24 (m, 8 H), 7.12 (d,  $J$  = 6.0 Hz, 8 H), 7.07-7.02 (m, 8 H), 2.50 (s, 6 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  152.26, 148.51, 147.49, 140.43, 140.02, 132.75, 130.95, 129.48, 128.07, 125.05, 123.52, 122.40, 20.55. HRMS (M+1) = 645.3003 (calc. 645.3018).

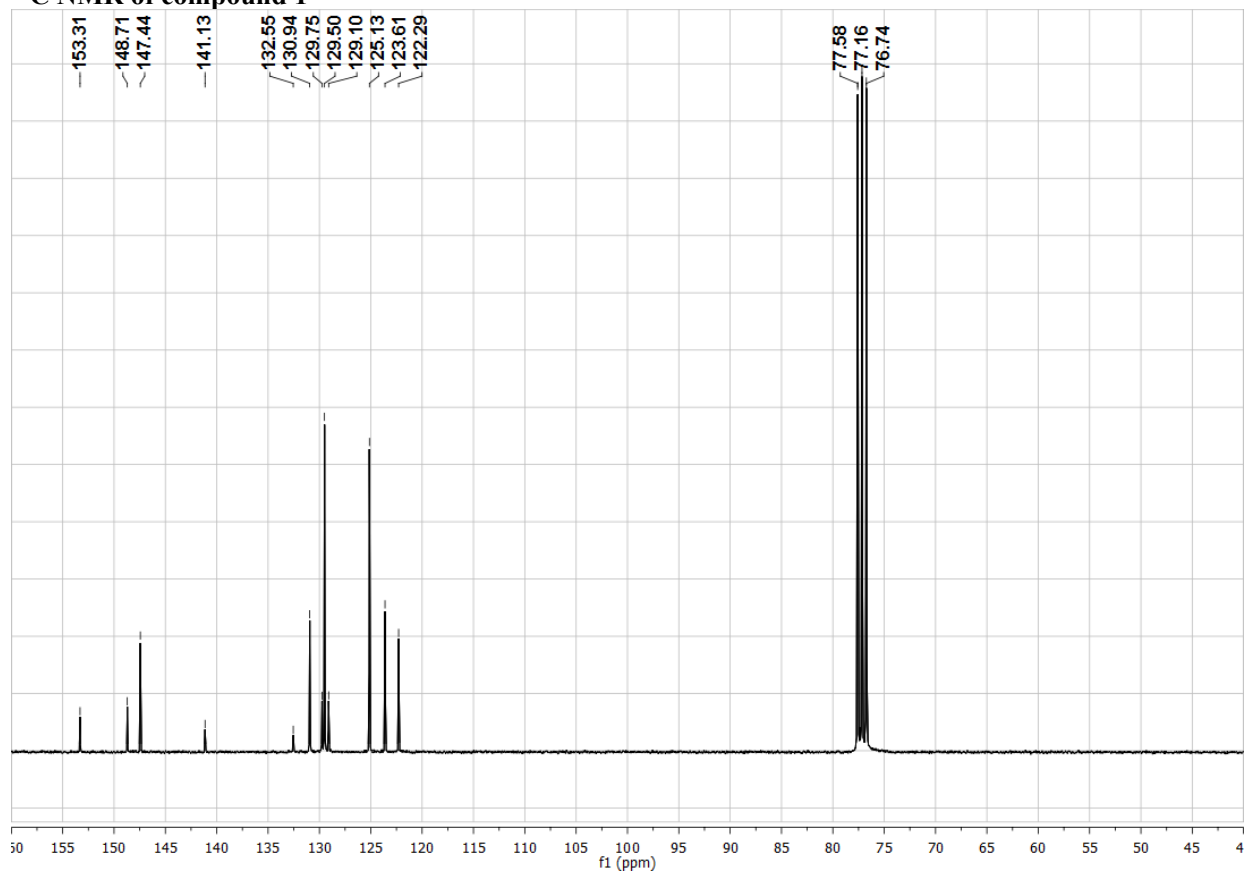
#### **Synthesis of compound 2,3-bis(4-diphenylamino-phenyl)-5,6-(9,10-dioxo-9,10-dihydro-anthracenyl)pyrazine (**3**)**

The procedure was the same with above except that 4,5-Dimethyl-1,2-phenylenediamine was replaced by 1,2-Diaminoanthraquinone (238 mg, 1.0 mmol). This reaction gave compound **3** (549 mg, yield 89%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.58 (d, 1 H), 8.41 (d, 1 H), 8.34-8.28 (m, 2 H), 7.86-7.75 (m, 4 H), 7.63 (m, 2 H), 7.33-7.26 (m, 8 H), 7.16 (d,  $J$  = 9.0 Hz, 8 H), 7.12 (d,  $J$  = 6.0 Hz, 4 H), 7.08 (d,  $J$  = 3.0 Hz, 2 H), 7.04 (d,  $J$  = 3.0 Hz, 2 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  183.88, 183.64, 154.91, 153.89, 149.72, 149.65, 147.19, 147.12, 142.94, 138.53, 135.34, 135.10, 134.75, 134.58, 133.60, 132.42, 131.53, 130.98, 132.19, 129.61, 129.57, 129.23, 127.50, 126.78, 126.37, 125.58, 125.56, 124.11, 124.00, 121.61, 121.52. HRMS (M+1) = 747.2766 (calc. 747.2760).

### <sup>1</sup>H NMR of compound 1



### <sup>13</sup>C NMR of compound 1



# HRMS of compound 1

## Elemental Composition Report

Page 1

### Single Mass Analysis

Tolerance = 15.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

1 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

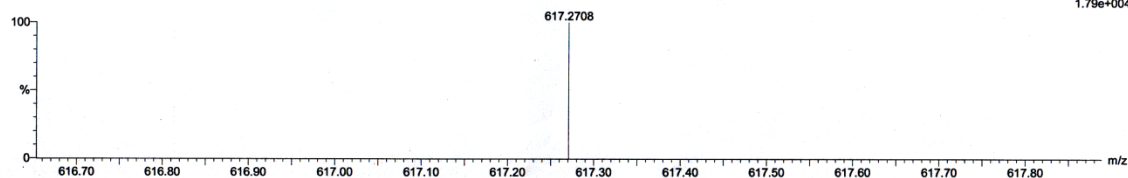
Elements Used:

C: 0-44 H: 0-33 N: 0-4

C44H32N4

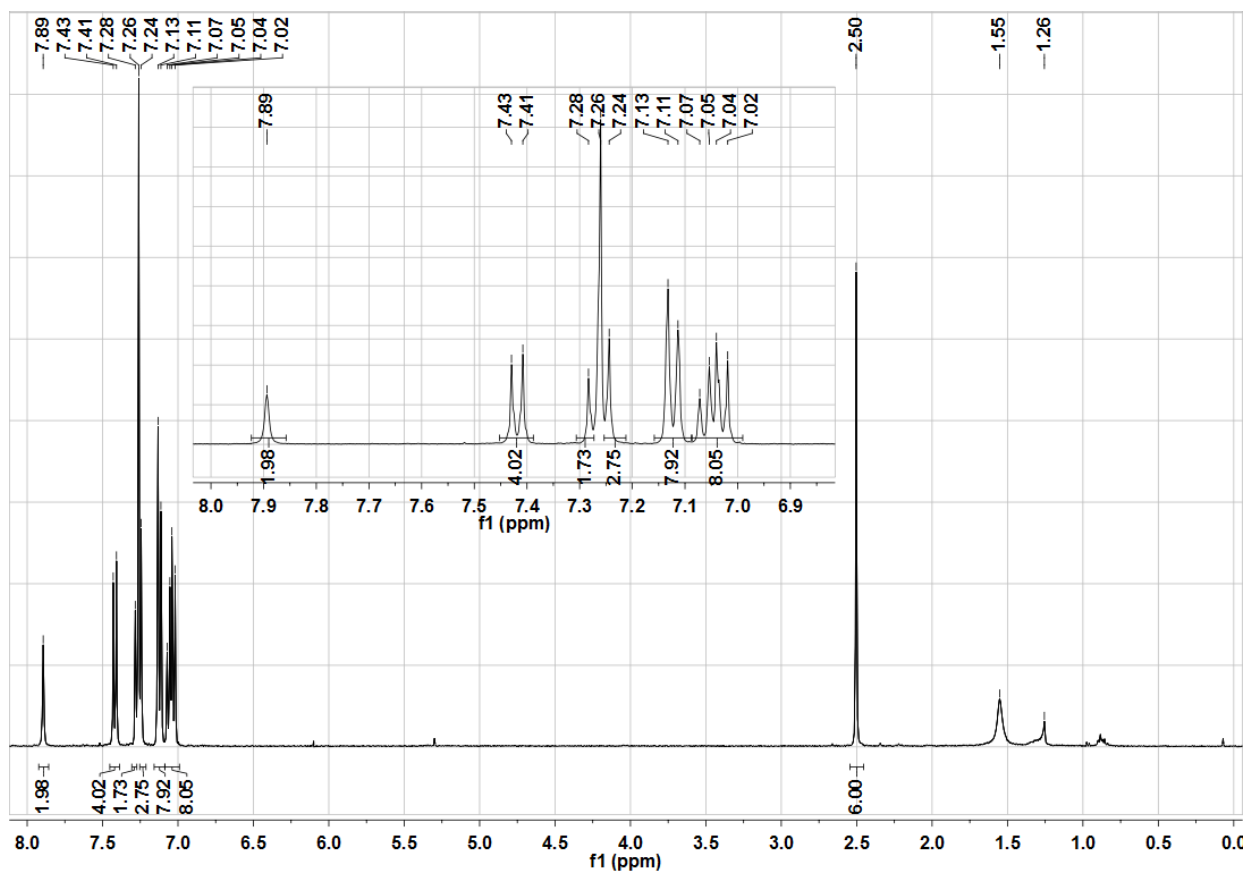
XL-2 3 (0.082) Cm (1:8)

1: TOF MS ES+  
1.79e+004

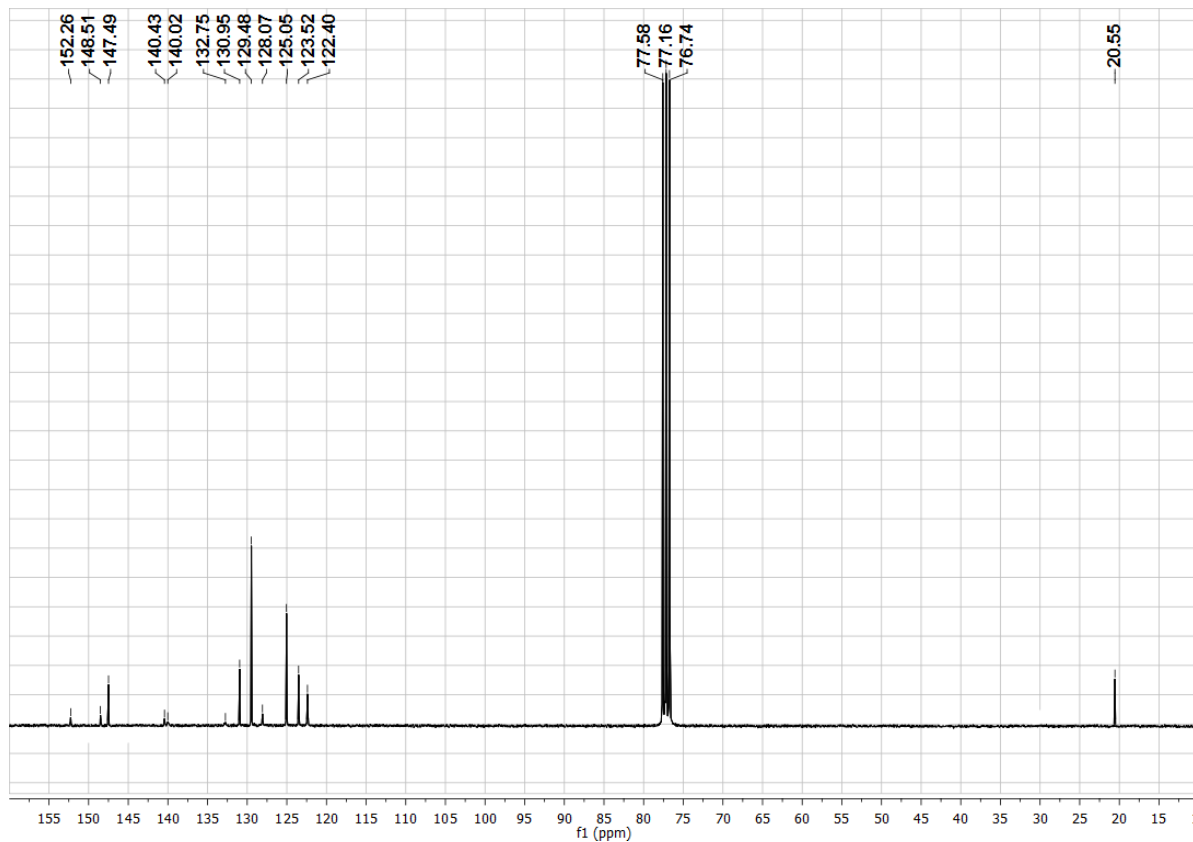


Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
617.2708	617.2705	0.3	0.5	30.5	32.1	0.0	C44 H33 N4

## <sup>1</sup>H NMR of compound 2



### <sup>13</sup>C NMR of compound 2



### HRMS of compound 2

#### Elemental Composition Report

Page 1

#### Single Mass Analysis

Tolerance = 15.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

1 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

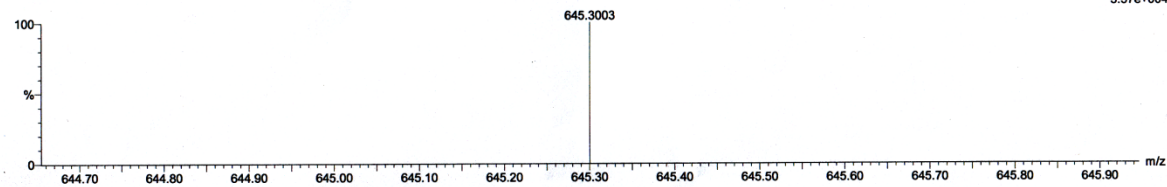
Elements Used:

C: 0-46 H: 0-37 N: 0-4

C<sub>46</sub>H<sub>36</sub>N<sub>4</sub>

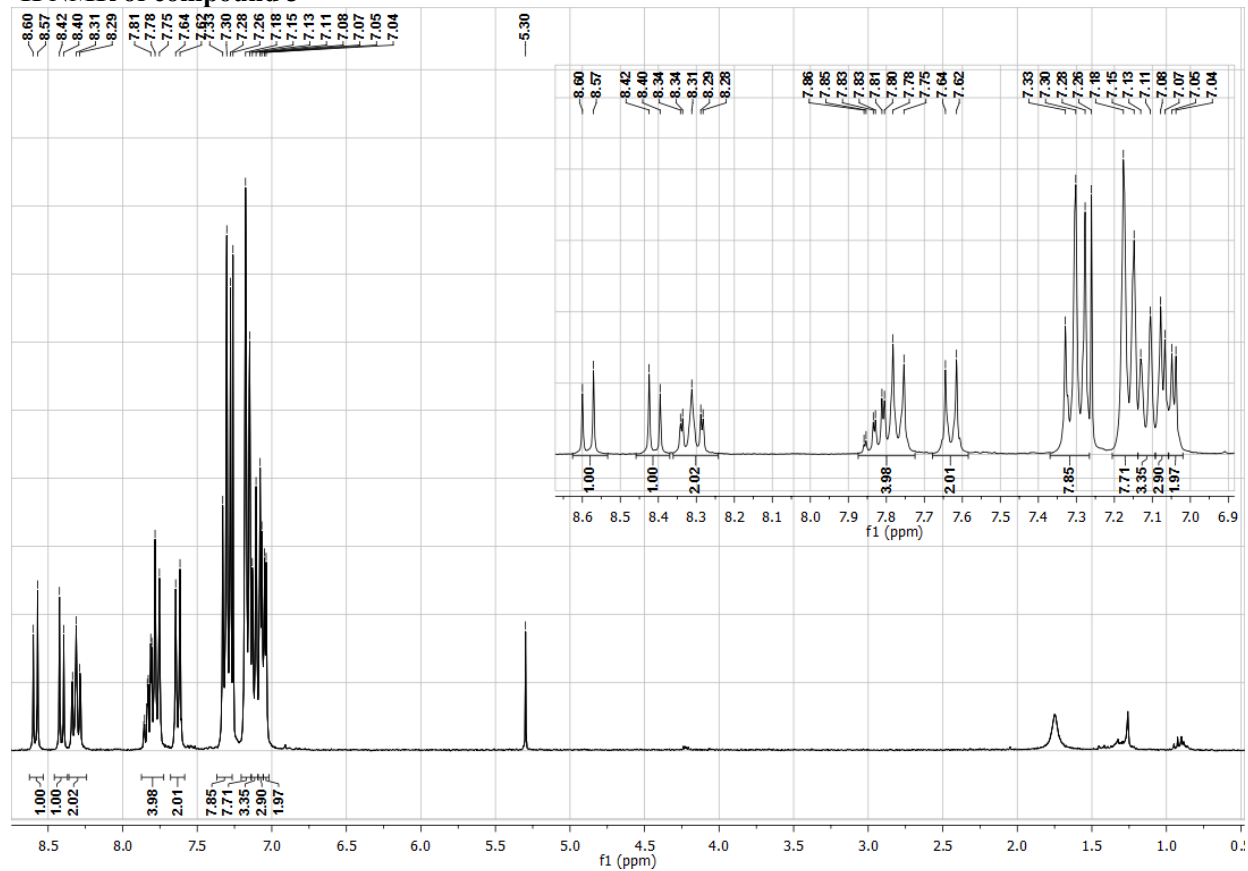
XL-3 3 (0.083) Cm (1:6)

1: TOF MS ES+  
3.37e+004

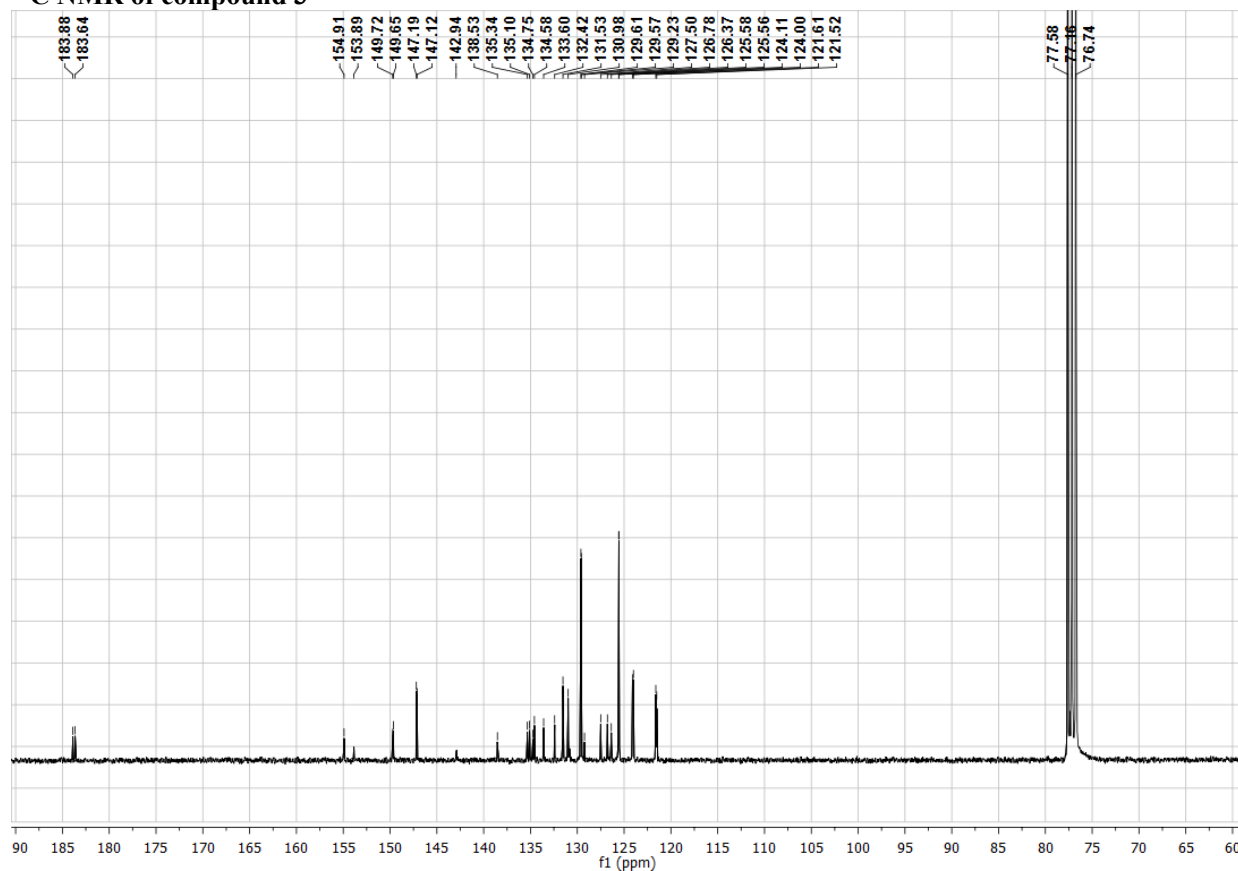


Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
645.3003	645.3018	-1.5	-2.3	30.5	33.8	0.0	C <sub>46</sub> H <sub>37</sub> N <sub>4</sub>

# <sup>1</sup>H NMR of compound 3



### <sup>13</sup>C NMR of compound 3



### HRMS of compound 3

#### Elemental Composition Report

Page 1

#### Single Mass Analysis

Tolerance = 15.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

2 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

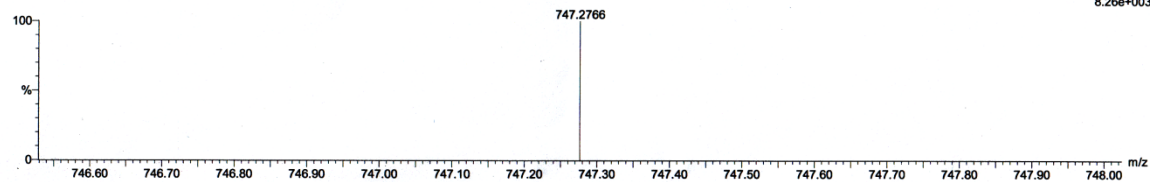
Elements Used:

C: 0-52 H: 0-35 N: 0-4 O: 0-2

C52H34N4O2

XL-5.3 (0.082) Cm (1:36)

1: TOF MS ES+  
8.26e+003



Minimum:  
Maximum:

100.0	15.0	-1.5
		50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
747.2766	747.2760	0.6	0.8	37.5	30.4	0.0	C52 H35 N4 O2

## S2. Photophysical properties

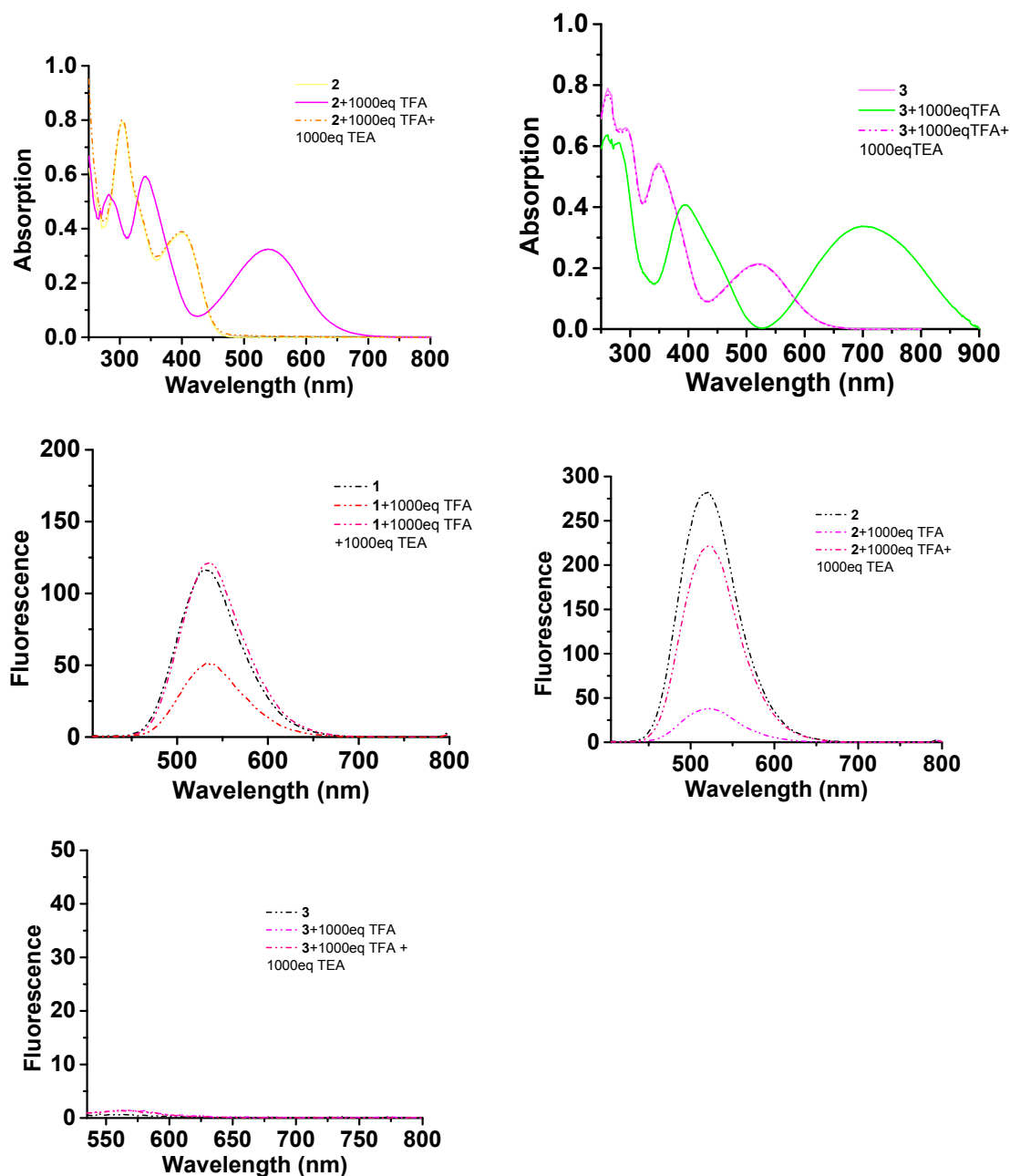


Figure S2 The UV-Vis and fluorescence spectra of compounds 1-3 upon adding 1000 eq TFA and TEA

## S3. Calculation

All the studied compounds 1-3 exhibit aromatic character, and the protonated species (compounds 1(H<sup>+</sup>), 2(H<sup>+</sup>) and 3(H<sup>+</sup>)) also keep the aromatic nature. Thus the positive charge mainly de-localized on the quinoxaline (compounds 1 and 2) and anthracene-9,10-dione (compound 3) units. This is also consistent with the calculated results. The excess charges upon protonation were analyzed through mulliken population analysis. As shown in Figure S3-1 and Table S3-1, we have summarized the mulliken charges for several important sites with excess positive charges ( $q > 0.3 e$ ).



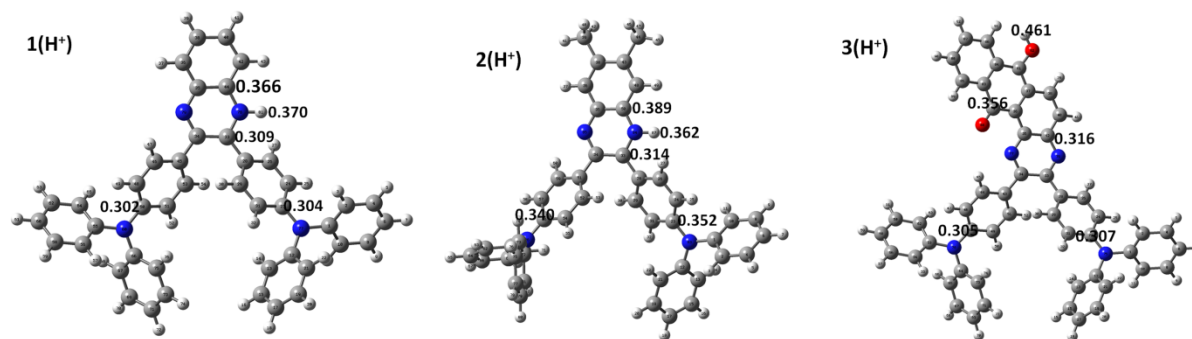


Figure S3-1 The important sites with excess positive charges ( $q > 0.3 e$ ) after protonation for compounds 1-3

Table S3-1. The important sites with excess positive charges ( $q > 0.3 e$ ) after protonation for compounds 1-3.

sites	23	33	44	50	81
<b>1(H<sup>+</sup>)</b>	0.304	0.309	0.366	0.302	0.370
sites	23	33	56	50	81
<b>2(H<sup>+</sup>)</b>	0.352	0.314	0.340	0.389	0.362
sites	23	42	48	79	93
<b>3(H<sup>+</sup>)</b>	0.307	0.316	0.305	0.356	0.461

The Gibbs free energies of protonation was determined at the B3LYP level (Table S3-2)

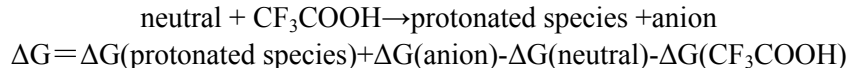


Table S3-2 Gibbs free energies of protonation

$\Delta G$ /a.u.	Neutral	CF <sub>3</sub> COOH	protonated species	Anion	G/kcal/mol
1	-1914.41	-526.77	-1914.80	-526.24	87.89
2	-1993.00	-526.77	-1993.39	-526.24	85.99
3	-2370.86	-526.77	-2371.23	-526.24	103.84

#### S4. NLO devices

The excitation source was a mode-locked Ti-sapphire oscillator-seeded regenerative amplifier (Spectra-Physics), which generates laser pulses centered at 800nm with pulse duration of ~100fs, working at a repetition rate of 1kHz. The laser beam was focused with a focal length of 125mm, producing a beam waist of ~20 $\mu$ m. A cuvette with 1mm optical path containing the solution of molecules was mounted on a translational stage (Newport), which moved along the direction of beam propagation in and out of focus. The transmittance of solutions was measured as a function of excitation power density, varying by moving translational stage.

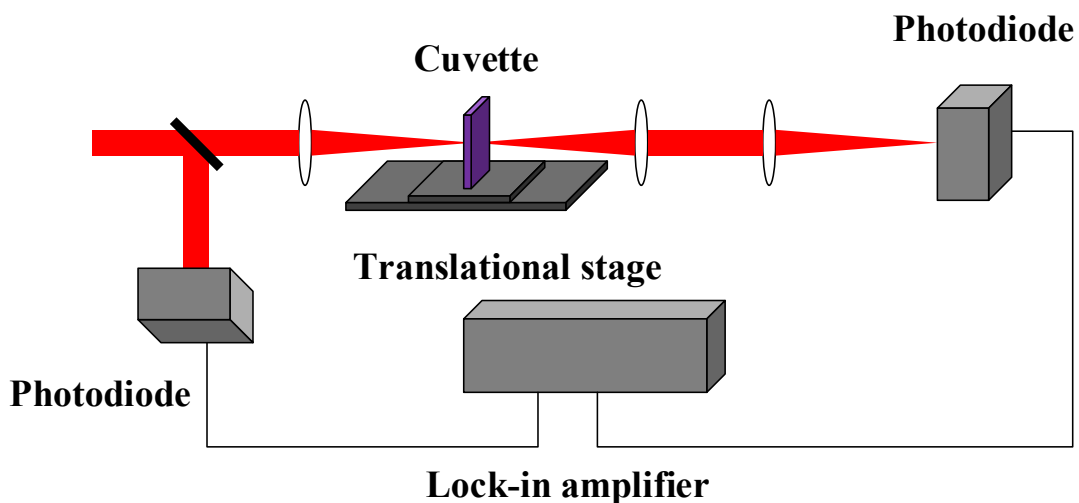


Figure S4-1 Schematic experimental setup of femtosecond open aperture z-scan measurement

By considering both RSA and SA, the total absorption coefficient is given by:

$$\alpha(I) = \frac{\alpha_0}{1 + I/I_s} + \beta I$$

Where  $\alpha_0$  is the linear absorption coefficient,  $I_s$  is saturation intensity,  $\beta$  is nonlinear absorption coefficient. A positive  $\beta$  describes the two photon absorption (2PA) of the molecules, while,  $\beta$  is negative in the case of SA. As shown in the UV-Vis absorption spectra of the compounds 1-3, the linear absorption is rather low, thus the first term is omitted in this work.

The nonlinear absorption coefficient  $\beta$  is determined by the transition dipole moment and the energy offset  $\Delta$ . In this work, compound 1, 2 and 3 possess a HOMO-LUMO gap of 3.11 eV, 3.19 eV and 2.12 eV, respectively. The HOMO and LUMO of the compounds are the ground state and intermediate state in the energy diagram, respectively. The excitation light generates a virtual state at 1.55 eV (corresponding to 800 nm excitation) above the ground state. A smaller  $\Delta$  value (but  $\Delta \neq 0$ ) would result in a larger nonlinear absorption coefficient and thus 2PA cross section. Compound 3 possesses a smaller  $\Delta$  (0.57 eV) compared to compound 1 and 2 (1.64 and 1.56 eV), thus possesses a larger 2PA cross section.

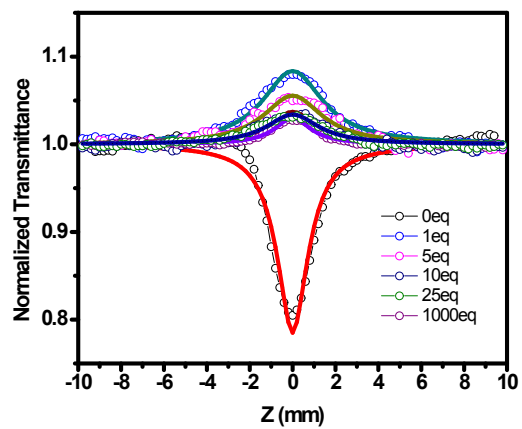
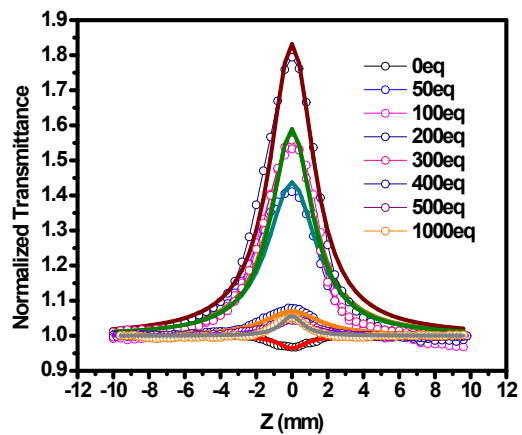
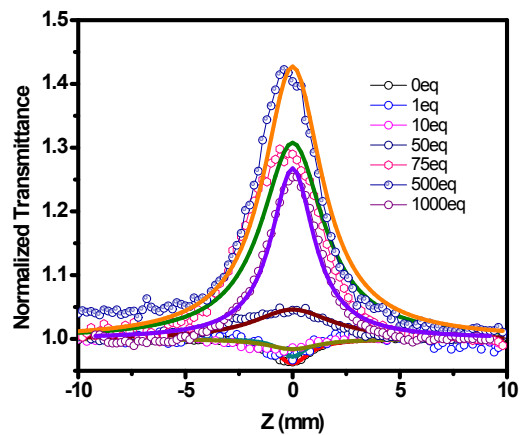


Figure S4-2 TFA concentration dependence Z-scan measurement for compounds 1, 2 and 3