

Electronic Supplementary Information

Green fluorescent naphthalene diimide: conducting layered hierarchical 2D nanosheets and reversible probe for detection of aromatic solvents

M. Pandeewar and T. Govindaraju*

Bioorganic Chemistry Laboratory, New Chemistry Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P.O., Bangalore 560064, India. Fax: +91 80 22082627; E-mail: tgraju@jncasr.ac.in

Contents

Experimental section

Materials and methods

Synthetic procedure and characterization

LD spectra of 1A and 1B in aqueous solution

FESEM and fluorescence confocal micrographs of 1B

Optical micrographs of 1A

PXRD analysis

¹H NMR and ¹³C NMR spectra of 1A

GC-MS and HRMS spectra of 1A

References

1. Materials and methods

Materials: 1,4,5,8-naphthalenetetracarboxylic acid dianhydride (NDA), *N,N*-diisopropylethylamine were obtained from Sigma-Aldrich, 1-hydroxybenzotriazole, L-alanine, D-alanine, and ethyl amine from Spectrochem Pvt. Ltd. (Mumbai, India). All other reagents and solvents were of reagent grade and used without further purification.

Absorption Spectroscopy: UV–vis spectra were recorded on a Perkin Elmer Model Lambda 900 spectrophotometer by using quartz cuvette of 1 mm path length.

Fluorescence Spectroscopy: Fluorescence spectra were recorded on a Perkin Elmer Model LS 55 spectrophotometer by using quartz cuvette of 1 mm path length. All fluorescence spectra with excitation wavelength $\lambda_{\text{ex}} = 360$ nm.

Circular Dichroism (CD): CD measurements were carried out on a Jasco J-815 spectro polarimeter under nitrogen atmosphere by using quartz cuvette of 1 mm path length.

For thin film CD measurements, the samples were prepared by drop casted the aqueous solutions onto a quartz plate and dried in air followed by vacuum drying at room temperature.

NMR Spectroscopy: ^1H and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer with chemical shifts reported as ppm (in CDCl_3 with tetramethylsilane as internal standard).

Mass Spectrometry (MS): Mass spectra were obtained from Shimadzu, GCMS-QP 2010 plus Gas chromatograph mass spectrometer and HRMS on Agilent Technologies 6538 UHD Accurate-Mass Q-TOF LC/MS spectrometer.

Field Emission Scanning Electron Microscopy (FESEM): FESEM images were acquired with a FEI Nova nanoSEM-600 equipped with a field-emission gun operating at 15 kV. The samples

were prepared by drop casted the aqueous solutions onto a Si (111) substrate and dried in air followed by vacuum drying at room temperature.

Atomic Force Microscopy (AFM): AFM images were acquired under ambient conditions using an Innova (Veeco) atomic force microscope in dynamic force (tapping) mode. The samples were prepared by drop casted the aqueous solutions onto a Si (111) substrate and dried in air followed by vacuum drying at room temperature. AFM section analysis was done offline.

Fluorescence confocal microscopy: Fluorescence confocal microscopy images were obtained from LSM 510 META-Carl Zeiss. A two-photon laser was employed to excite the self-assembled **1a** and **1b** nanosheets. The LSM image examiner was utilized for processing the images.

Powder X-ray Diffraction (PXRD): PXRD patterns were recorded with a Rigaku-99 (Miniflex) diffractometer using Cu K α radiation ($\lambda=1.5406$ Å). The samples were prepared by drop casted the aqueous solutions onto a glass slide and allowed to dry in air followed by vacuum drying at room temperature. The diffraction peaks were indexed with the TREOR 90 program.¹

Scanning tunnelling microscopy (STM): STM measurements were performed on a Bruker diInnova scanning probe microscope. The samples were prepared by drop casting the aqueous solution of **1a** onto a HOPG and allowed to dry in air followed by vacuum drying at room temperature. Measurements were performed under ambient conditions using mechanically cut Pt/Ir wire from several points on the nanosheets of different topographical thickness with set point of 1 nA and a bias voltage of 500 mV was used.

Experimental section

General procedure for the synthesis of amino acid methylester.

Anhydrous methanol (50 mL) was placed into a 100 mL two necked round-bottom flask, fitted with a reflux condenser and an additional dropping funnel and cooled to ice temperature. Acetyl chloride (3 mL) was added drop-wise through the dropping funnel. After 15 min, alanine (6.9 g, 18.16 mmol) was added, and the reaction mixture was refluxed overnight at 70 °C. The reaction mixture was dried in vacuo to obtain alanine methylester hydrochloride in quantitative yield and used for further reaction without purification.

General procedure for the Synthesis of 1A and 1B.²

1,4,5,8-Naphthalenetetracarboxylic dianhydride (NDA) (0.5 g, 1.86 mmol) was suspended in 450 mL of isopropanol. α -Alanine methylester (0.26 g, 1.86 mmol) and ethylamine (0.1 mL, 1.86 mmol) were added to the mixture, followed by *N,N*-diisopropylethylamine (6.4 mL, 37 mmol). The mixture was allowed to reflux for 24 h. After cooling to room temperature, the resulting precipitate was filtered and washed with water. The organic layer was separated, dried under vacuo and the residue was purified by column chromatography (CH₂Cl₂/ MeOH: 10/1).

Characterization data for 1A. Yield 58 %. ¹H NMR (CDCl₃, 400 MHz) δ_{H} 8.77 (4H, d), 5.76 (1H, q), 4.27 (2H, q), 3.75 (3H, s), 1.72 (3H, dd), 1.36 (3H, t); ¹³C NMR (CDCl₃, 400 MHz) δ_{C} 170.3, 162.5, 162.3, 131.3, 130.9, 126.9, 126.7, 126.6, 126.3, 52.6, 49.6, 36.1, 14.8, 13.3.
HRMS: 381.1063 [M+H]⁺, calcd. 381.1087 for C₂₀H₁₇N₂O₆. GCMS: 380 [M]⁺, calcd. 380.3 for C₂₀H₁₆N₂O₆.

Characterization data for 1B. Yield 58 %. ¹H NMR (CDCl₃, 400 MHz) δ_{H} 8.76 (4H, d), 5.76 (1H, q), 4.27 (2H, q), 3.75 (3H, s), 1.72 (3H, dd), 1.36 (3H, dt); ¹³C NMR (CDCl₃, 400 MHz) δ_{C}

170.4, 162.8, 162.6, 131.4, 130.9, 126.8, 126.7, 126.4, 126.3, 52.7, 49.7, 36.2, 14.9, 13.4.

HRMS: 381.1058 [M+H]⁺, calcd. 381.1087 for C₂₀H₁₇N₂O₆. GCMS: 380 [M]⁺, calcd. 380.3 for

C₂₀H₁₆N₂O₆.

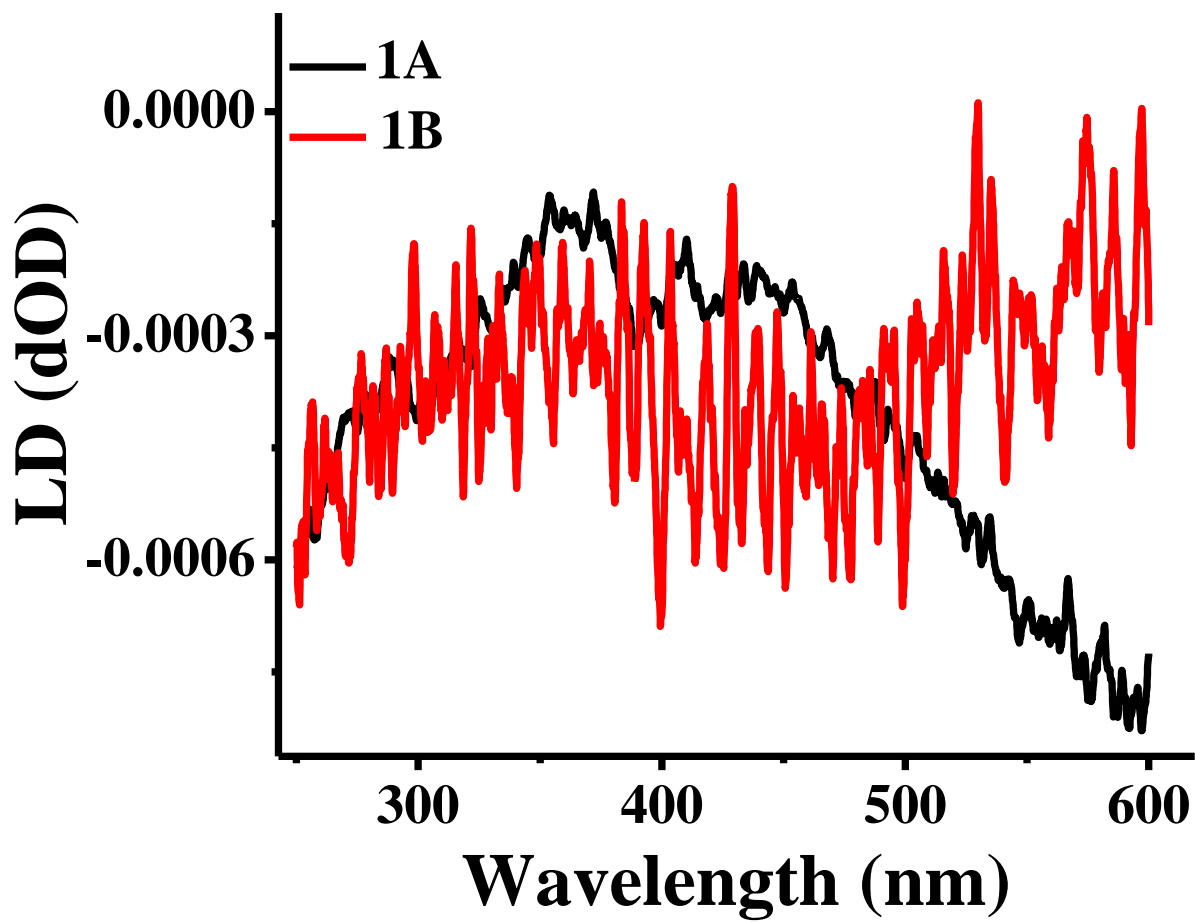


Fig. S1 Linear dichroism (LD) spectra of **1A** and **1B** in aqueous solution (no LD artifacts was observed).

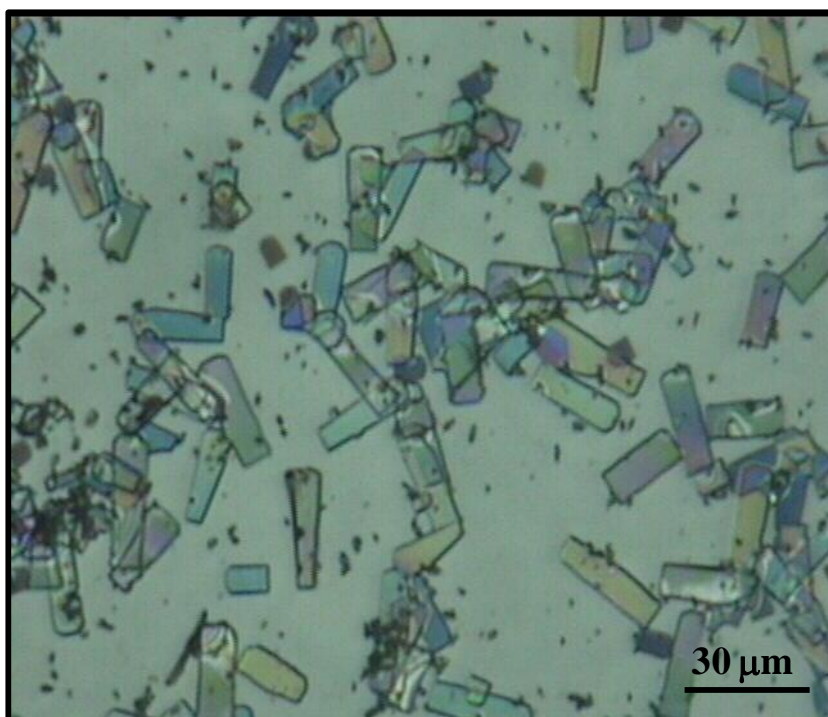


Fig. S2 Optical image of nanosheets of **1A** (aqueous solution drop-casted on Si (111) substrate).

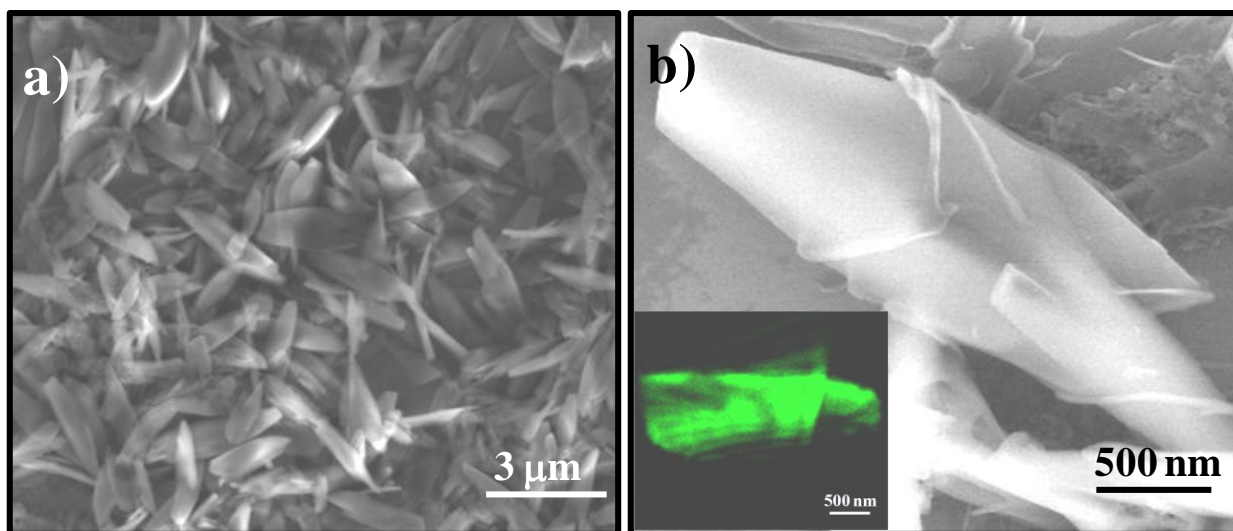


Fig. S3 (a) FESEM images of folded nanosheets of **1B**. (b) High resolution FESEM image of individual folded nanosheet of **1B**, inset: fluorescence confocal micrograph of folded nanosheet of **1B**.

Indexing result of the powder pattern of 1A³ MONOCLINIC SYSTEM

$a=20.0759 \text{ \AA}$, $b=6.4481 \text{ \AA}$, $c=18.8193 \text{ \AA}$

$\alpha=90.000$, $\beta=104.473$, $\gamma=90.000$, VOLUME=2358.89

H	K	L	SST-OBS	SST-CALC	DELTA	2TH-OBS	2TH-CALC	D-OBS	FREE
-1	0	1	0.00253	0.00252	1.20E-05	5.769	5.755	15.3072	0
2	0	0		0.00628			9.091		
-2	0	1	0.00645	0.00639	5.40E-05	9.211	9.172	9.5932	0
1	0	2	0.01043	0.01039	3.40E-05	11.722	11.703	7.5436	0
1	1	0	0.0159	0.01584	6.20E-05	14.489	14.461	6.1083	0
0	1	1		0.01606			14.56		
0	0	3		0.01608			14.572		
1	0	3	0.02012	0.02016	-4.70E-05	16.309	16.328	5.4308	0
2	1	1	0.02393	0.02401	-8.10E-05	17.799	17.829	4.9793	0
3	0	2	0.02635	0.0263	4.80E-05	18.685	18.668	4.7451	0
3	1	0	0.02839	0.0284	-1.00E-05	19.402	19.405	4.5714	0
0	0	4		0.02859			19.47		
4	0	1		0.03026			20.036		
0	1	3	0.03032	0.03035	-3.50E-05	20.055	20.067	4.4239	0
			0.03533			21.669		4.098	
3	0	3		0.03775			22.408		
-4	1	1	0.03786	0.03783	2.80E-05	22.44	22.432	3.9588	0
-5	0	2		0.03803			22.491		
-4	1	2	0.03983	0.03984	-1.30E-05	23.025	23.028	3.8596	0
-2	1	4	0.04248	0.04244	3.90E-05	23.79	23.779	3.7372	0
-2	0	5		0.04258			23.818		

			0.04834			25.401		3.5036	0
					-1.15E-				
-5	0	4	0.05099	0.0511	04	26.1	26.13	3.4114	0
-5	1	1		0.05113			26.137		
4	0	3		0.05126			26.17		
-4	1	4		0.05459			27.023		
					-3.60E-				
5	0	2	0.05474	0.05478	05	27.062	27.071	3.2923	0
2	0	5	0.05933	28.196					
					-3.90E-				
5	1	1	0.05946	0.0595	05	28.228	28.237	3.1589	0
-1	2	1	0.0596	28.262					
					-9.60E-				
-1	2	2	0.06403	0.06413	05	29.315	29.338	3.0441	0
0	2	2		0.06423			29.362		
0	0	6		0.06433			29.386		
					1.00E-				
5	1	2	0.06905	0.06905	06	30.47	30.469	2.9314	0
-4	0	6	0.06936	30.539					
					2.30E-				
-2	2	3	0.07445	0.07442	05	31.668	31.663	2.8232	0
-2	1	6	0.07484	31.753					
					-2.32E-				
-7	0	4	0.08186	0.08209	04	33.25	33.299	2.6923	0
-2	0	7		0.08212			33.305		
5	1	3		0.08217			33.316		
4	2	0		0.08221			33.323		

NUMBER OF OBS. LINES = 21

NUMBER OF CALC. LINES = 39

MEAN ABSOLUTE DISCREPANCIES

<Q> = .0000430

<DELTA(2-THETA)> = .015652

Indexing result of the powder pattern of 1B³

MONOCLINIC SYSTEM

$a=15.5447 \text{ \AA}$, $b=11.6472 \text{ \AA}$, $c=14.940590 \text{ \AA}$

$\alpha=90.000$, $\beta=102.270$, $\gamma=90.000$, VOLUME=2643.23

H	K	L	SST-OBS	SST-CALC	DELTA	2TH-OBS	2TH-CALC	D-OBS	FREE
1	0	0	0.00255	0.00257	-1.90E-05	5.792	5.814	15.2459	0
1	0	1	0.00651	0.00649	1.50E-05	9.254	9.244	9.5485	0
1	0	2	0.01609	0.01598	1.09E-04	14.575	14.526	6.0724	0
0	2	1		0.02028			16.374		
1	1	2	0.02035	0.02036	-3.00E-06	16.404	16.405	5.3994	0
1	2	1	0.02401	0.02399	2.50E-05	17.83	17.82	4.9708	0
			0.02657			18.761		4.726	
-2	0	3	0.02853	0.02852	8.00E-06	19.447	19.445	4.5608	0
-1	1	3		0.02859			19.469		
0	2	2		0.02863			19.484		
2	1	2	0.03041	0.03035	6.40E-05	20.086	20.064	4.4173	0
-2	2	2	0.03442	0.03437	5.30E-05	21.384	21.368	4.1519	0
-3	0	3	0.03798	0.03796	1.10E-05	22.475	22.472	3.9528	0
-3	2	1	0.03997	0.04001	-4.20E-05	23.066	23.078	3.8529	0
0	2	3		0.04255			23.809		
-1	0	4	0.04267	0.04256	1.10E-04	23.844	23.813	3.7288	0
0	1	4	0.04889	0.04892	-2.70E-05	25.548	25.556	3.4838	0
1	0	4	0.05165	0.05166	-1.00E-05	26.273	26.276	3.3893	0

-4	0	3		0.05255			26.506		
					-8.00E-				
4	1	1	0.05285	0.05285	06	26.581	26.583	3.3508	0
					-4.30E-				
2	2	3	0.05962	0.05966	05	28.265	28.276	3.1548	0
-5	0	2		0.06406			29.321		
5	0	0		0.06429			29.377		
					-5.50E-				
0	3	3	0.06437	0.06442	05	29.394	29.407	3.0362	0

NUMBER OF OBS. LINES = 17

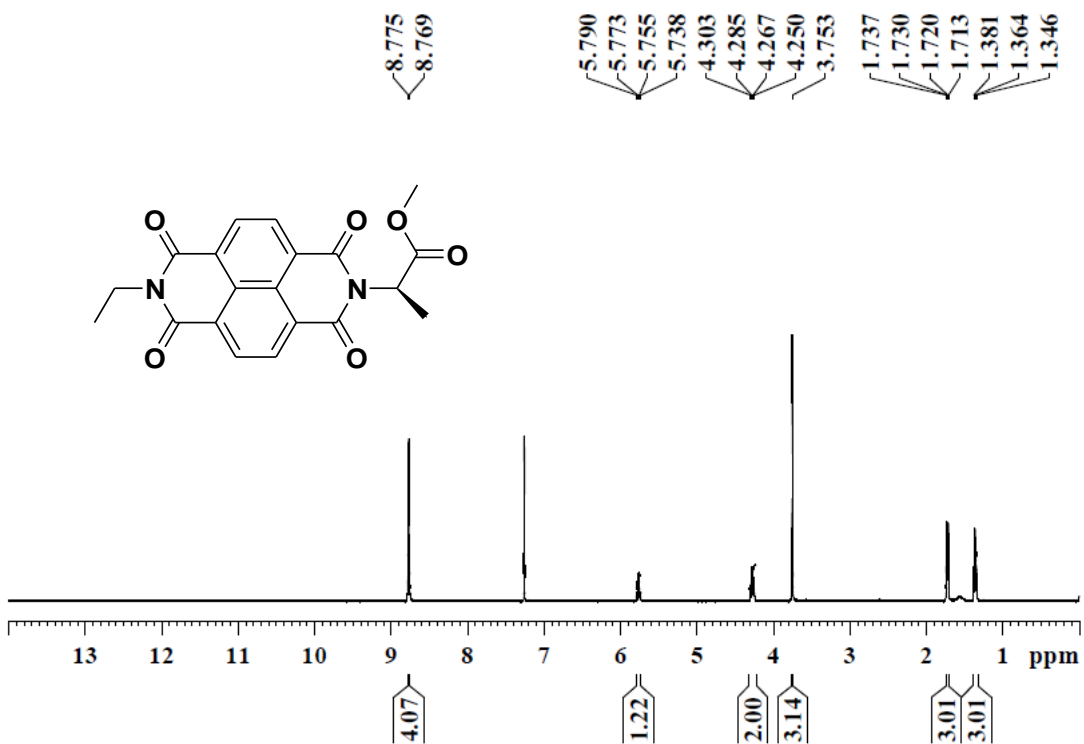
NUMBER OF CALC. LINES = 23

MEAN ABSOLUTE DISCREPANCIES

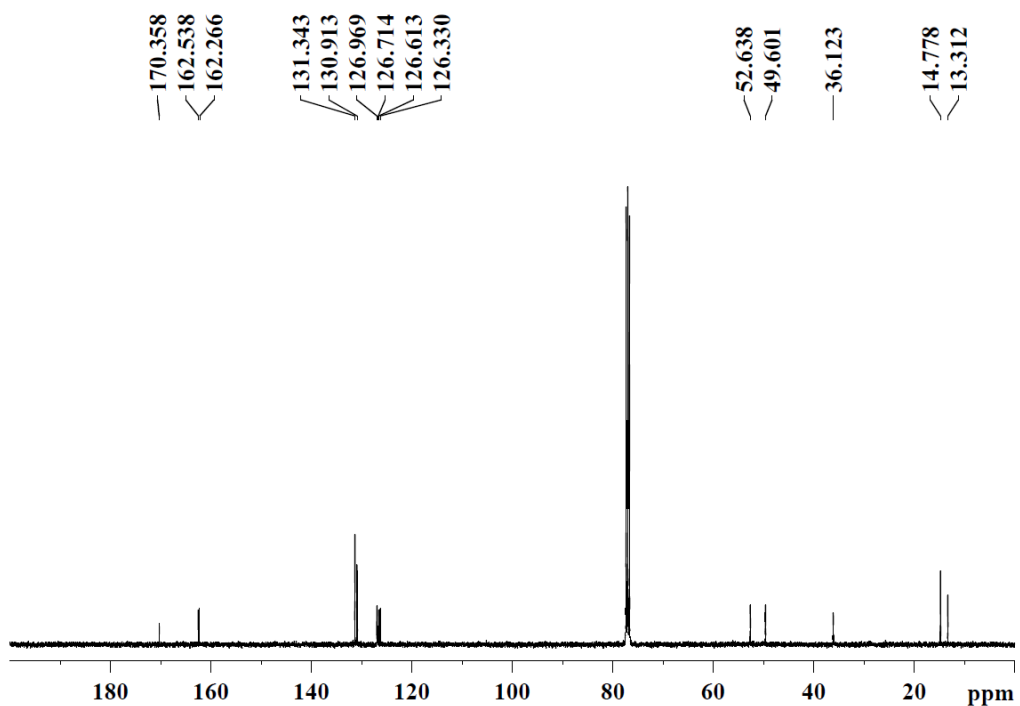
<Q> = .0000376

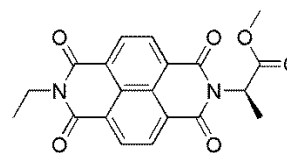
<DELTA(2-THETA)> = .013438

¹H NMR spectrum (CDCl₃, 400 MHz) of 1A



¹³C NMR spectrum (CDCl₃, 400 MHz) of 1A

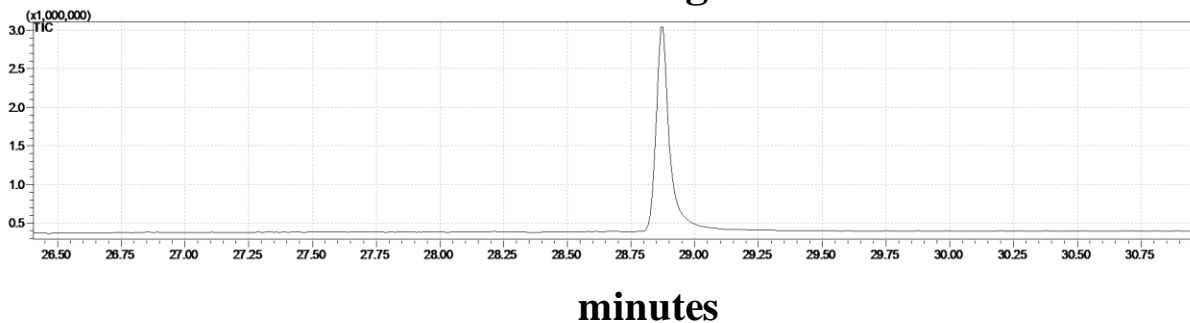




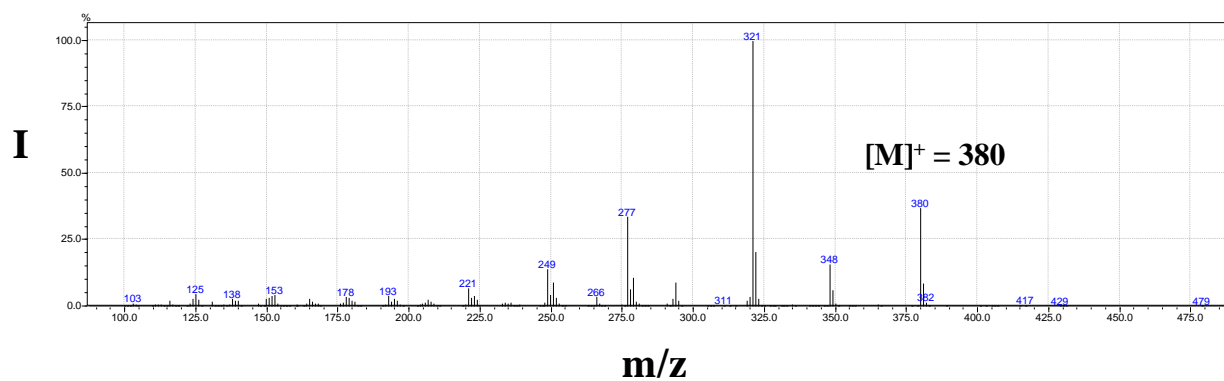
GC-MS of 1A

$C_{20}H_{16}N_2O_6$
Exact Mass: 380.1008

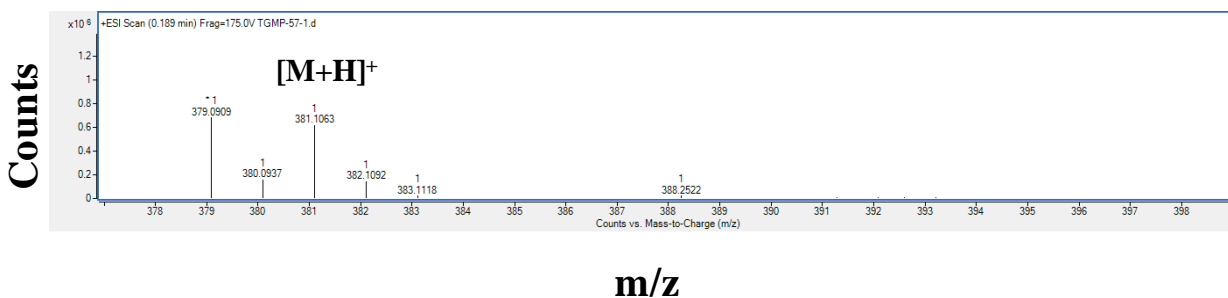
Chromatogram



Mass spectrum



HRMS of 1A



References

- 1 P. E. Warner, L. Eriksson, M. Westdahl, *J. Appl. Cryst.*, 1985, **18**, 367-370.
- 2 R. S. Lokey, Y. Kwok, V. Guelev, C. J. Pursell, L. H. Hurley, B. L. Iverson, *J. Am. Chem. Soc.*, 1997, **119**, 7202-7210.
- 3 (a) D. Louër, M. Louër, *J. Appl. Cryst.*, 1972, **5**, 271-275; (b) A. Boultif, D. Louër, *J. Appl. Cryst.*, 1991, **24**, 987-993.