Supporting Information

Defect-sensitive crystals based on diaminomaleonitrile-functionalized Schiff base with aggregation-enhanced emission

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Materials and Instrumentations

Ethanol and tetrahydrofuran (THF) were distilled from sodium benzophenoneketyl and magnesium, respectively, under nitrogen immediately prior to use. Other chemicals were purchased from Aldrich and Alfa Aesar and used as received without further purification. ^{1}H and ^{13}C spectra were measured on a Bruker AV 400 spectrometer in dimethylsulfoxide-d_6 (DMSO- d_6) using tetramethylsilane (TMS; δ= 0) as internal reference. High resolution mass spectra (HRMS) were recorded on a GCT premier CAB048 mass spectrometer operated in MALDI-TOF mode. UV spectra were measured on a Milton Roy Spectronic 3000 Array spectrophotometer. Photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer. The morphologies of the nanoaggregates of A3MN were investigated using JOEL 2010 Transmission Electron Microscopy (TEM). Powder X-ray diffraction (XRD) patterns were recorded on an X'pert PRO, PANalytical diffractometer. Fluorescent image of A3MN single crystals was recorded under an Olympus CKX41 phase contrast microscope (Olympus, Japan) and a Nikon A1 confocal laser scanning microscope (CLSM, Nikon Corporation, Japan) at an excitation wavelength of 405 nm. Ultrasonic wave was generated by a Branson 5510 ultrasonic cleaner. Single crystals of A3MN were grown from THF and ethanol mixture at room temperature. X-ray diffraction (XRD) intensity data were collected at 173 K on a Bruker-Nonices Smart Apex CCD diffractometer with graphite monochromated Mo Kα radiation. Processing of the intensity data was conducted using the SANT and SADABS routines, and the structure and refinement were carried out using the SHELTL suite of X-ray programs (version 6.10). The OPTEP drawing of A3MN is given in Scheme 1 and its crystal data were summarized in Table S1 and S2. The ground-state geometries were optimized using the density functional (DFT) with B3LYP hybrid functional at the basis set level of 6-31G. All the calculations were performed using Gaussian 03 package.

Synthesis and Characterization of A3MN

A solution of diaminomaleonitrile (4 g, 37mmol) and 4-(diethylamino)benzaldehyde (6.4 g, 37 mmol) in dry EtOH (300 mL) was heated up to 50 ^{o}C for 6 h. After cooled to room temperature, the crude product was precipitated. After filtered and washed several times by EtOH, the crude product was recrystallized in THF/EtOH. The characterization data of A3MN are given as below.

2-Amino-3-((E)-(4-(diethylamino)benzylidene)amino)maleonitrile (A3MN).

^{1}H NMR (400 MHz, DMSO-d_6), δ (TMS, ppm): 8.08 (s, 1H), 7.80–7.78 (d, 1H), 7.41 (s, 2H), 6.71–6.69 (d, 2H), 3.45–3.40 (m, 4H), 1.11–1.10 (t, 6H).^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 155.4, 150.1, 131.2, 123.8, 122.3, 115.1, 114.1, 110.9, 104.5, 43.9, 12.4. HRMS (MALDI-TOF): m/z 268.1556 ([M+H]$^{+}$calcd 268.1484).

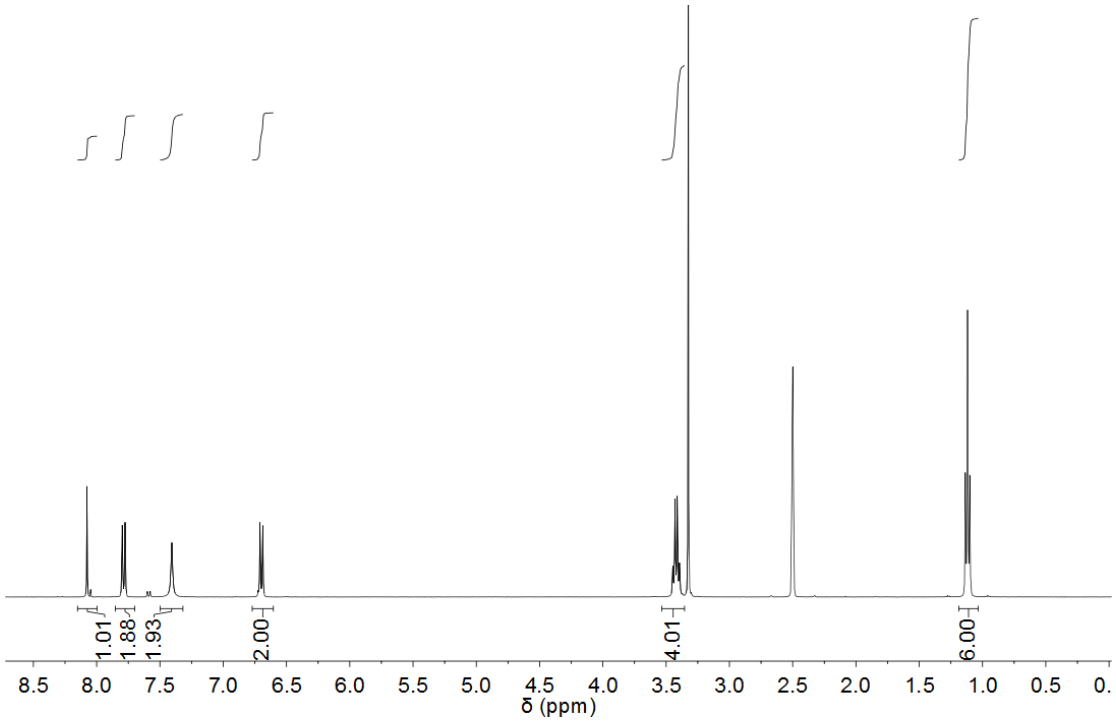

Fig. S1 ^{1}H NMR spectrum of A3MN.

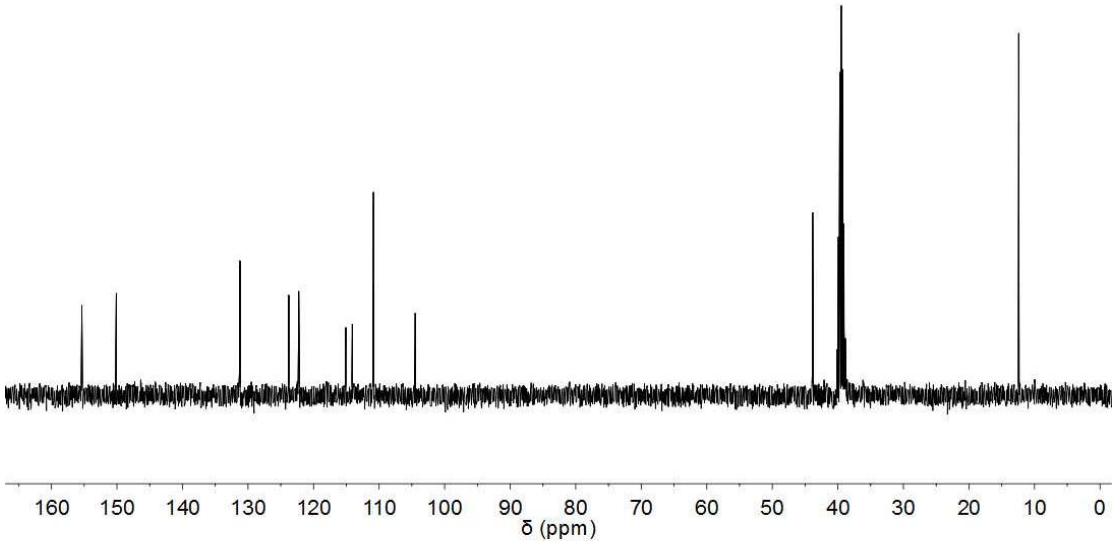

Fig. S2 ^{13}C NMR spectrum of A3MN.

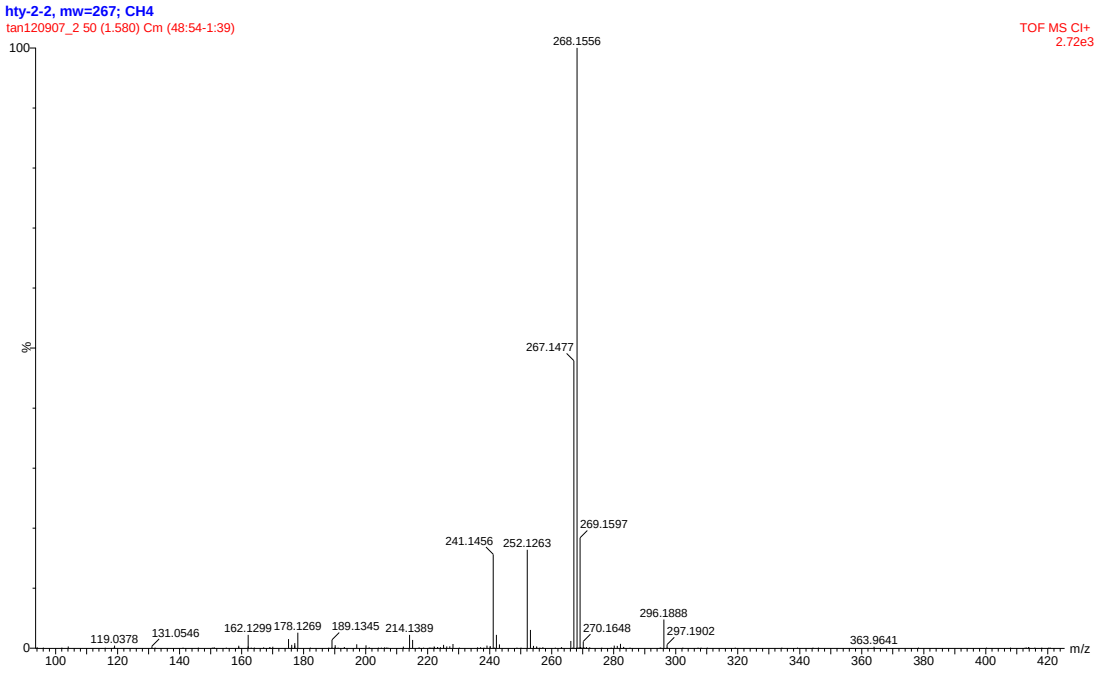

Fig. S3 High resolution mass spectrum of A3MN.

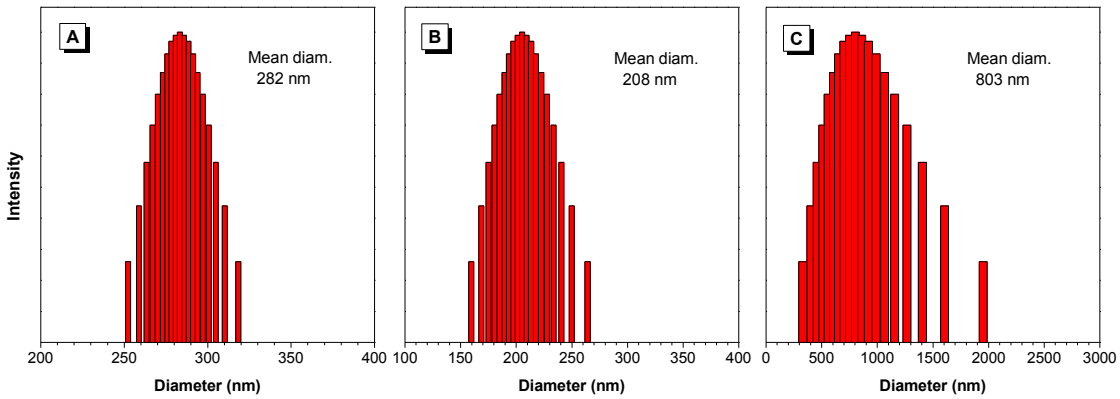

Fig. S4 Hydrodynamic diameter of A3MN at (A) 80, (B) 90 and (C) 99% water fraction in THF/water mixtures.

Table S1. Crystal data and structure refinement for A3MN.

Identification code	A3MN
Empirical formula	C15 H17 N5
Formula weight	267.34
Temperature	173.00(14) K
Wavelength	1.5418 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 9.4160(2) Å
	b = 12.7884(2) Å
	c = 12.9807(4) Å
Volume	1478.99(6) $Å^3$
Z	4
Density (calculated)	1.201 Mg/m^3
Absorption coefficient	0.602 mm^{-1}
F(000)	568
Crystal size	0.40 x 0.35 x 0.25 mm^3
Theta range for data collection	4.96 to 66.97 °.
Index ranges	-11<=h<=9, -15<=k<=11, -14<=l<=15
Reflections collected	7102
Independent reflections	2584 [R(int) = 0.0177]
Completeness to theta = 66.50 °	98.74 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.59148
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2584 / 0 / 183
Goodness-of-fit on F^2	1.003
Final R indices [I>2sigma(I)]	R1 = 0.0355, wR2 = 0.0999

Table S2. twistedangles ( ) for A3MN.

C(11)-N(1)-C(1)	120.80(8)
C(5)-N(5)-C(12)	121.71(9)
C(5)-N(5)-C(14)	121.97(9)
C(12)-N(5)-C(14)	116.32(9)
N(1)-C(1)-C(3)	121.72(9)
C(2)-C(1)-N(1)	117.78(9)
C(2)-C(1)-C(3)	120.48(9)
N(2)-C(2)-C(1)	123.25(9)
N(2)-C(2)-C(4)	117.31(9)
C(1)-C(2)-C(4)	119.42(9)
N(3)-C(3)-C(1)	174.91(11)
N(4)-C(4)-C(2)	176.92(11)
N(5)-C(5)-C(6)	121.10(9)
N(5)-C(5)-C(10)	121.92(9)
C(10)-C(5)-C(6)	116.98(9)
C(7)-C(6)-C(5)	121.36(9)
C(6)-C(7)-C(8)	121.54(9)
C(7)-C(8)-C(11)	122.41(9)
C(9)-C(8)-C(7)	117.12(9)
C(9)-C(8)-C(11)	120.47(9)
C(10)-C(9)-C(8)	122.14(9)
C(9)-C(10)-C(5)	120.86(9)
N(1)-C(11)-C(8)	122.53(9)
N(5)-C(12)-C(13)	113.93(9)
N(5)-C(14)-C(15)	113.38(10)

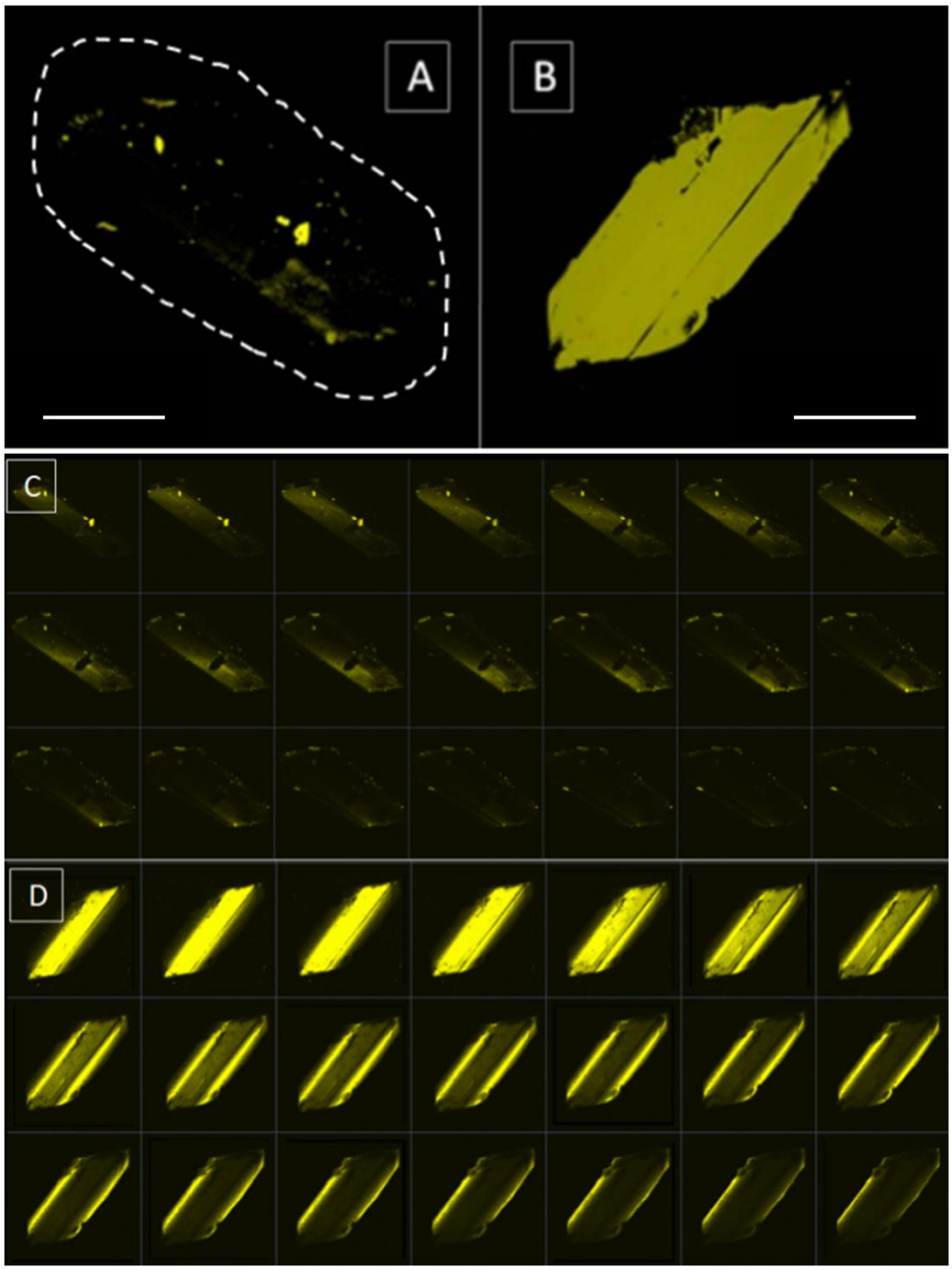

Fig. S5 Confocal image of single crystals of A3MN under UV illumination (A) before and (B) after acetone etching. Scale bar: 200 μm. (C, D) Z-stack mode scanning of the crystals shown in (A) and (B).

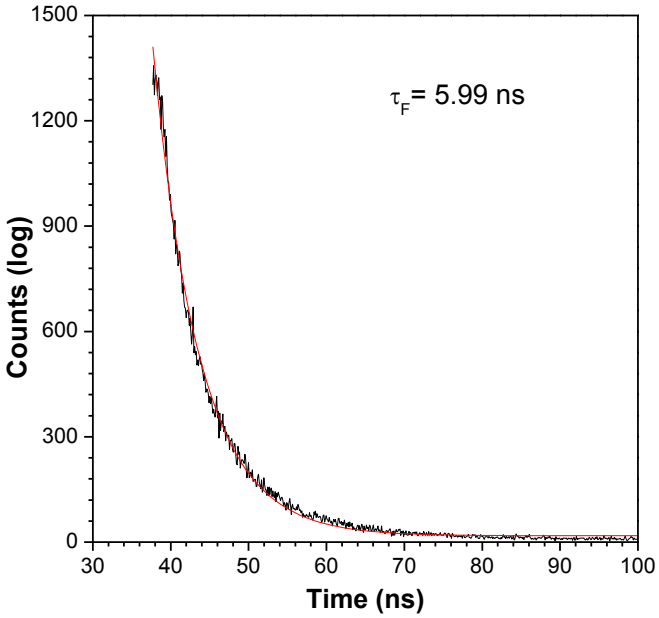

Fig. S6 Fluorescence lifetime decay curve of A3MN and its fitting to single-exponential decay function.