BEILSTEIN JOURNAL OF ORGANIC CHEMISTRY

Supporting Information

for

Preparation of anthracene-based tetraperimidine hexafluorophosphate and selective recognition of chromium(III) ions

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Supporting crystallographic data, fluorescence, UV, HRMS, and IR spectra of 3 and 3·Cr^{3+}, general considerations, characterization data, and copies of the ^{1}H and ^{13}C NMR spectra of all compounds

Table of contents

1. CCDC number for compound 3.

CCDC 1918752 contains the supplementary crystallographic data for compound The data can be obtained free of charge via http//www.ccdc.cam.ac.uk/conts/retrieving. html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: (+44) 223-336-033; or e-mail: deposit@ccdc.cam. ac. uk.

2. Crystal data and structure refinements for 3

Table S1: Crystal data and structure refinements for **3**

Chemical formula	$C_{76}H_{76}N_{10}P_4F_{24}$ ·$4CH_3CN$	F(000)	968
Formula weight	1875.57	Cryst size, mm	0.25 × 0.15 × 0.14
Cryst syst	Triclinic	θ_{min}, θ_{max}, deg	3.74, 67.06
Space group	$P\bar{1}$	T /K	172.9(1)
a/Å	11.850(5)	No. of data collected	14087
b/Å	12.401(6)	No. of unique data	7439
c/Å	14.951(5)	No. of refined params	579
α/deg	92.4(1)	Goodness-of-fit on F^2 [a]	1.048
β/deg	94.3(1)	Final R indices[b] [$I > 2\sigma(I)$]	
γ/deg	107.3(4)	R_1	0.0754
V/Å^3	2086.65(1)	wR_2	0.1986
Z	1	R indices (all data)	
D_{calcd}, Mg/m^3	1.493	R_1	0.1117
Abs coeff, mm^{-1}	1.797	wR_2	0.2238

[a] $GOF = [\Sigma\omega(F_o^2 - F_c^2)^2 /(n - p)]^{1/2}$, where n is the number of reflection and p is the number of parameters refined. [b] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/ \Sigma w(F_o^2)^2]^{1/2}$.

3. Crystal packing of compound 3

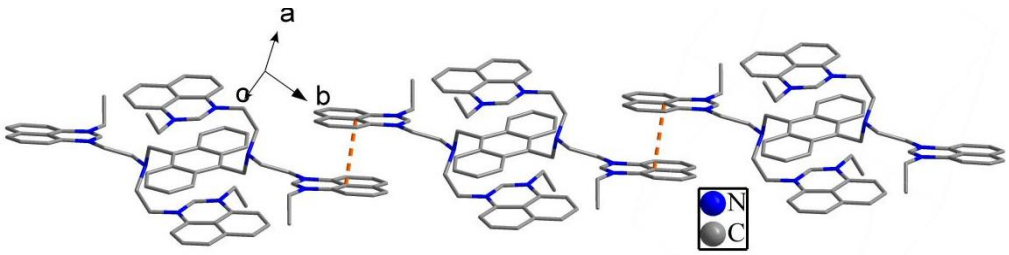

Figure S1(a): 1D supermolecular chain of **3**.

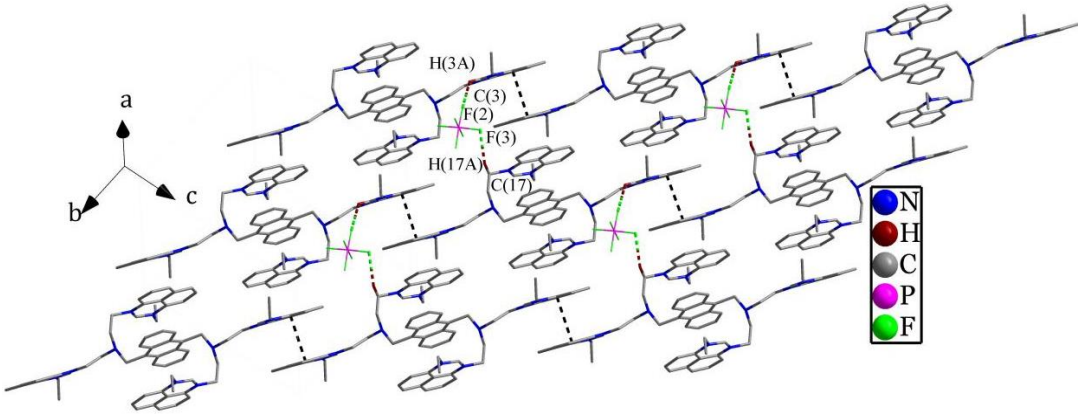

Figure S1(b): 2D supermolecular layer of **3.**

4. Fluorescence and UV–vis spectroscopy for compound 3

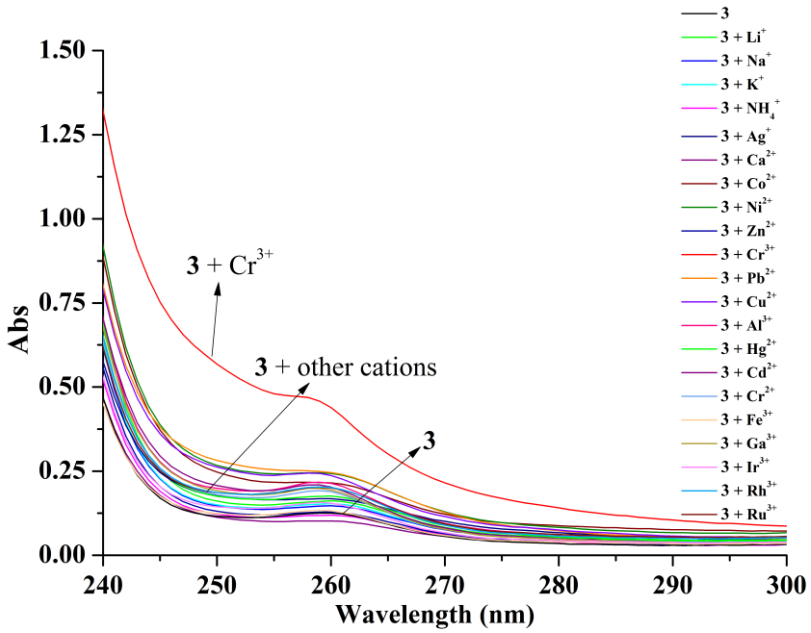

Figure S2: UV–vis absorption change of **3** (5.0×10^{-6} mol/L) upon the addition of the nitrate salts of K^+, Na^+, Li^+, Ag^+, NH_4^+, Zn^{2+}, Cd^{2+}, Ca^{2+}, Ni^{2+}, Pb^{2+}, Cu^{2+}, Co^{2+}, Al^{3+}, Cr^{3+}, Hg^+, Hg^{2+}, Rh^{3+}, Ir^{3+}, Cr^{2+}, Ga^{3+}, Ru^{3+} and Fe^{3+} (5×10^{-5} mol/L) in acetonitrile at 25 °C.

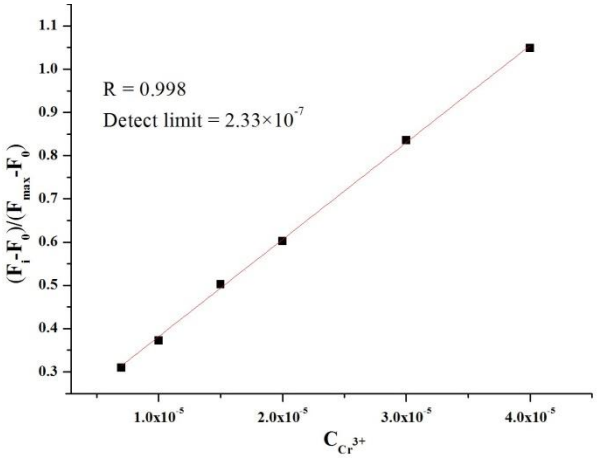

Figure S3: Emission (at 423 nm) of **3** at different concentrations of Cr^{3+} (0.7, 1.0, 1.5, 2.0, 3.0, 4.0 × 10^{-5} mol/L) added, normalized between the minimum emission (0.0 M Cr^{3+}) and the emission 4.0 × 10^{-5} mol/L Cr^{3+}. The detection limit was determined to be 2.33 × 10^{-7} mol/L.

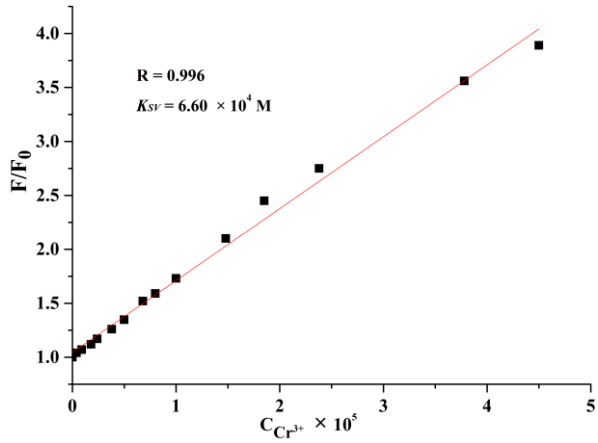

Figure S4: Stern–Volmer plot of **3** (5.0 × 10^{-6} mol/L) in the presence of Cr^{3+} in CH_3CN/DMSO 9:1 (v:v) at 25 °C, and the linear range is from 0.0–4.5 × 10^{-5} mol/L.

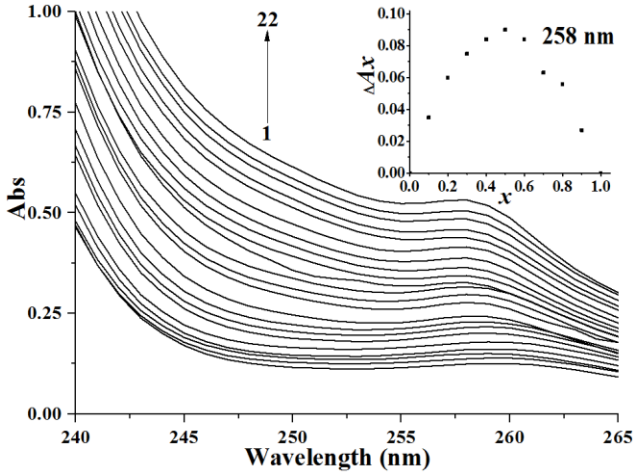

Figure S5: The UV–vis absorption spectra of **3** (5.0 × 10^{-6} mol/L) in CH_3CN/DMSO

9:1 (v/v) at 25 °C. $C_{Cr^{3+}}$ for curves 1–22 are 0, 0.02, 0.06, 0.1, 0.2, 0.4, 0.6, 0.8, 1.2, 1.4, 1.6, 1.8, 2.0, 2.2, 2.4, 2.6, 2.8, 3.0, 3.2, 3.4, 3.5 and 3.6×10^{-5}. Inset: the Job's plot for **3**·Cr^{3+} complex in CH_3CN/DMSO 9:1 (v/v) at 258 nm.

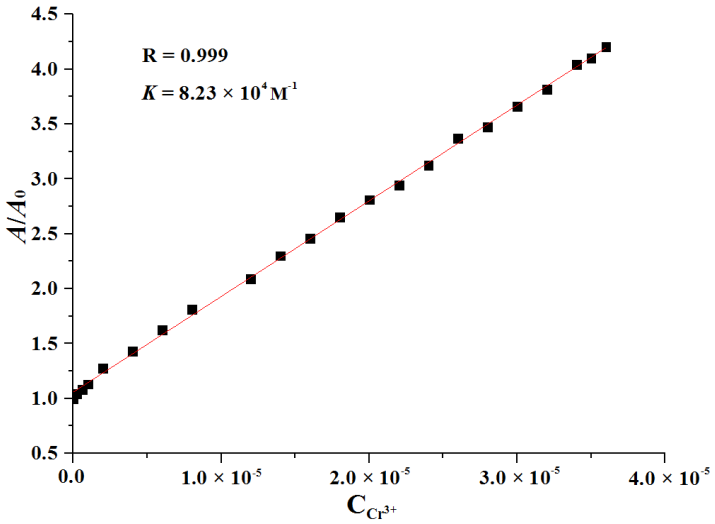

Figure S6: Benesi–Hildebrand plot of **3** (5.0×10^{-6} mol/L) at 258 nm in the presence of Cr^{3+} in CH_3CN/DMSO 9:1 (v/v) at 25 °C.

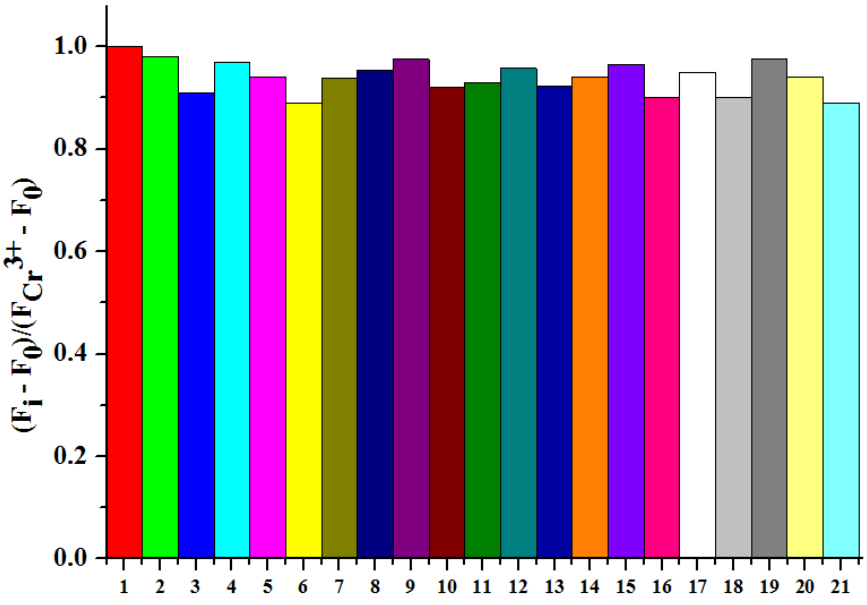

Figure S7: Change ratio $((F_i - F_0)/(F_{Cr^{3+}} - F_0))$ of fluorescence intensity of **3** (5.0×10^{-6} mol/L) at 423 nm upon the addition of 30 equiv Cr^{3+} in the presence of 30 equiv background cations. 1: Cr^{3+}; 2: Cr^{3+} + Li^+; 3: Cr^{3+} + Na^+; 4: Cr^{3+} + K^+; 5: Cr^{3+} + NH_4^+; 6: Cr^{3+} + Ag^+; 7: Cr^{3+} + Ca^{2+}; 8: Cr^{3+} + Co^{2+}; 9: Cr^{3+} + Ni^{2+}; 10: Cr^{3+} + Zn^{2+}; 11: Cr^{3+} + Cu^{2+}; 12: Cr^{3+} + Cd^{2+}; 13: Cr^{3+} + Pb^{2+}; 14: Cr^{3+} + Hg^{2+}; 15: Cr^{3+} + Al^{3+}; 16: Cr^{3+} +

Rh^{3+}; 17: Cr^{3+} + Ir^{3+}; 18: Cr^{3+} + Cr^{2+}; 19: Cr^{3+} + Ga^{3+}; 20: Cr^{3+} + Ru^{3+}; 21: Cr^{3+} + Fe^{3+} in CH_3CN/DMSO 9:1 (v/v) at 25 °C.

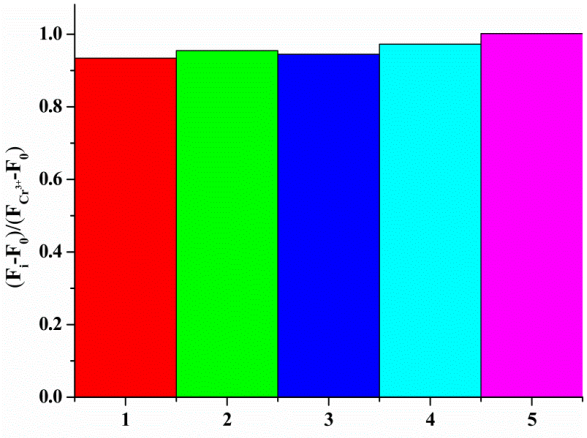

Figure S8: Fluorescence intensity of **3** (5.0 × 10^{-6} mol/L) in various mixtures of different Cr^{3+} salts (1: $CrCl_3$, 2: $CrBr_3$, 3: $Cr_2(SO_4)_3$, 4: $Cr(OAc)_3$, 5: $Cr(NO_3)_3$; 3.0 × 10^{-6} mol/L) in CH_3CN/DMSO 9:1 (v/v) at 25 °C.

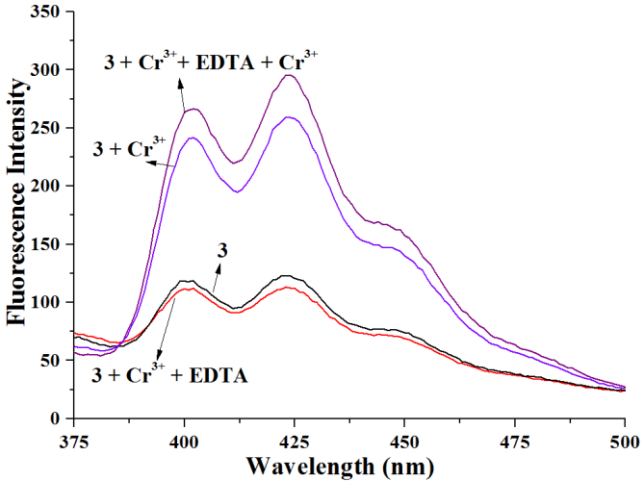

Figure S9: Fluorescence reversibility of **3** upon the detection of Cr^{3+}. Fluorescent changes of **3** after the addition of Cr^{3+}, EDTA, Cr^{3+} in that order in CH_3CN/DMSO 9:1 (v/v) at 25 °C.

5. The Figure S10 π_{13}^{15} bond of perimidine

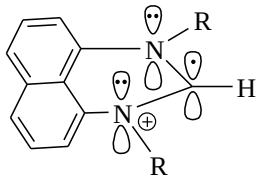

Figure S10: π_{13}^{15} bond of perimidine.

6. Figure of HRMS for 3·Cr^{3+}

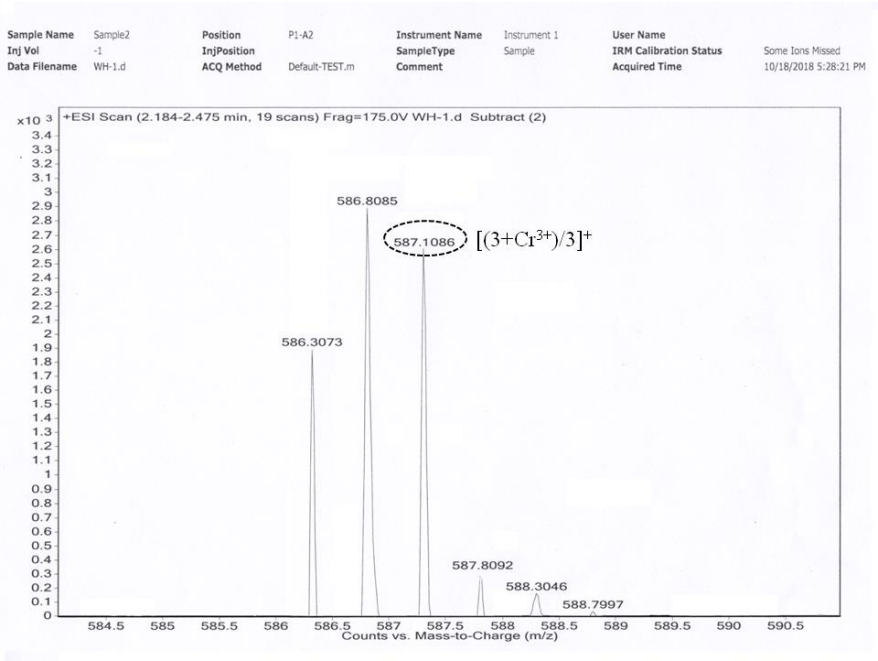

Figure S11: HRMS for **3**·Cr^{3+}.

7. Infrared spectra of 3 and 3·Cr^{3+}

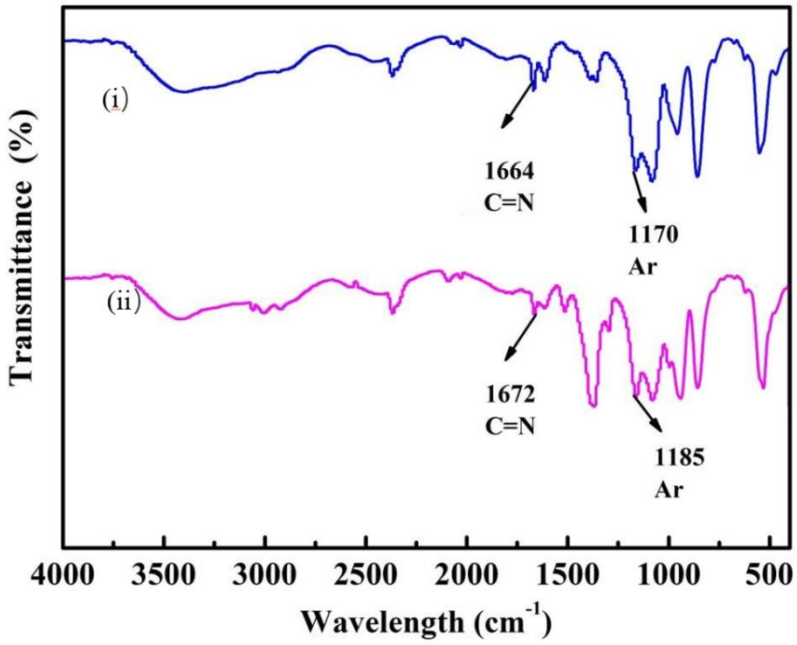

Figure S12: Infrared spectroscopy of **3** (top) and **3**·Cr^{3+} (bottom).

8. Figure of HRMS for 3

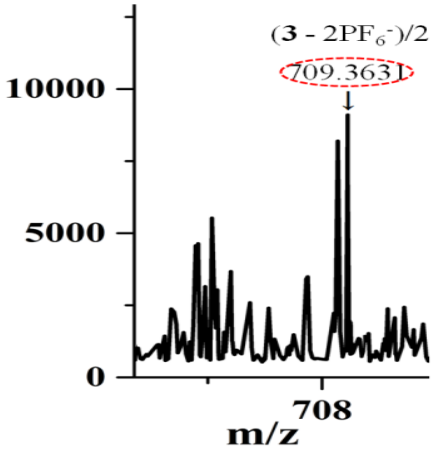

Figure S13: HRMS for **3**.

9. ^{1}H NMR and ^{13}C NMR spectra of intermediate and compound 3

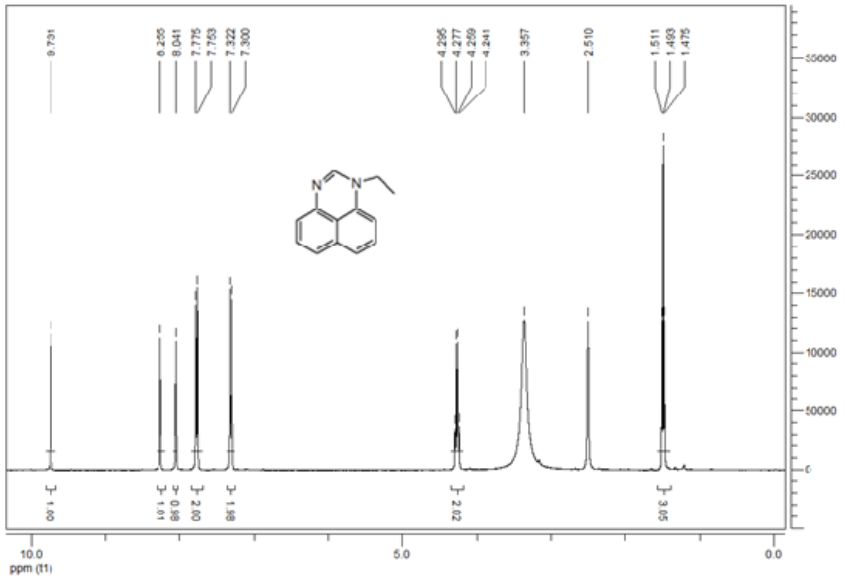

Figure S14: The ^{1}H NMR (400 MHz, DMSO-d_6) spectra of 1-ethylperimidine.

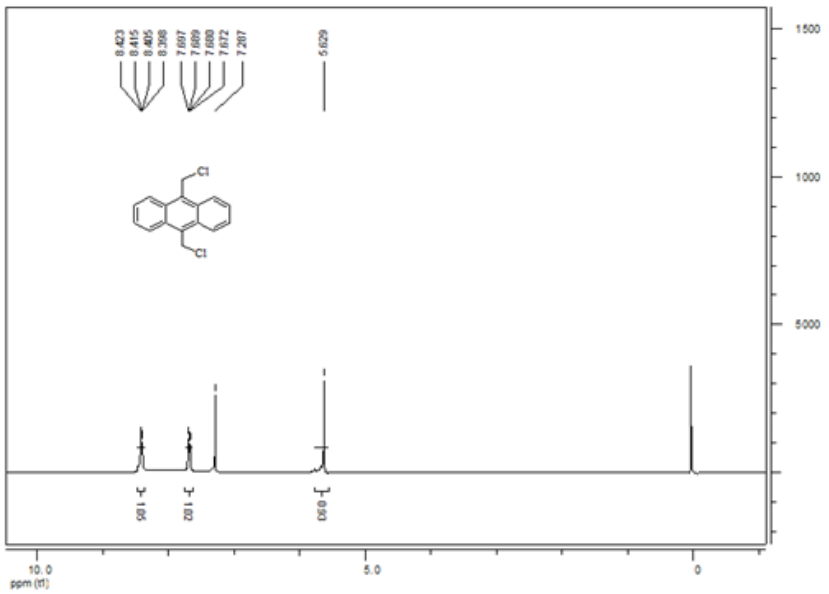

Figure S15: The ^{1}H NMR (400 MHz, $CDCl_3$) spectra of 9,10-bis(chloromethyl)anthracene.

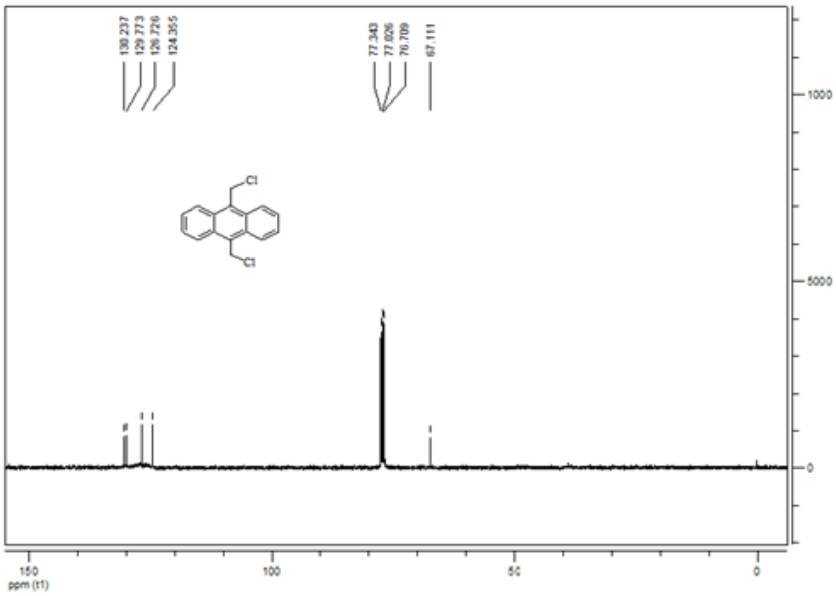

Figure S16: The ^{13}C NMR (100 MHz, $CDCl_3$) spectra of 9,10-bis(chloromethyl)anthracene.

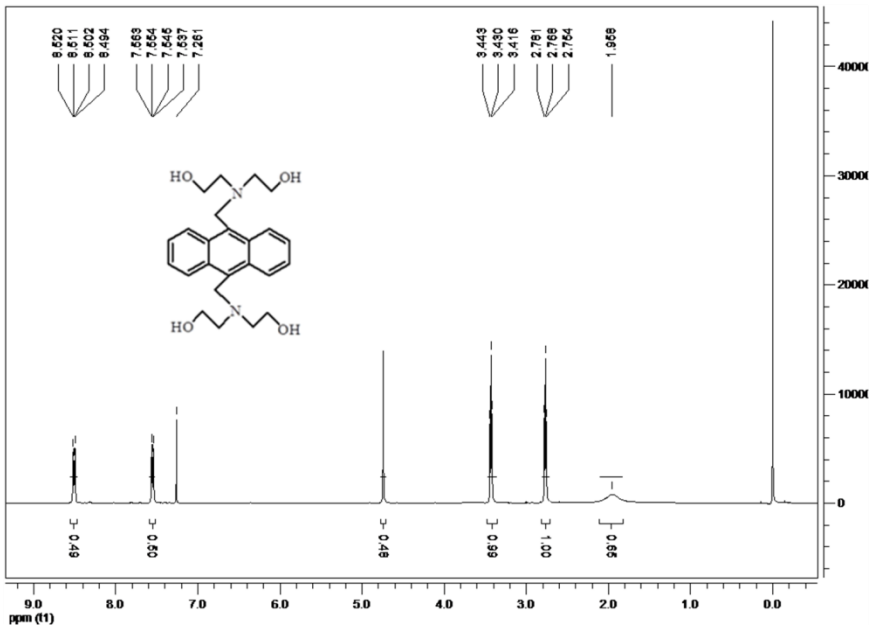

Figure S17: The ^{1}H NMR (600 MHz, $CDCl_3$) spectra of 9,10-bis[{*N*,*N*-di(2-hydroxyethyl)amino}methyl]anthracene.

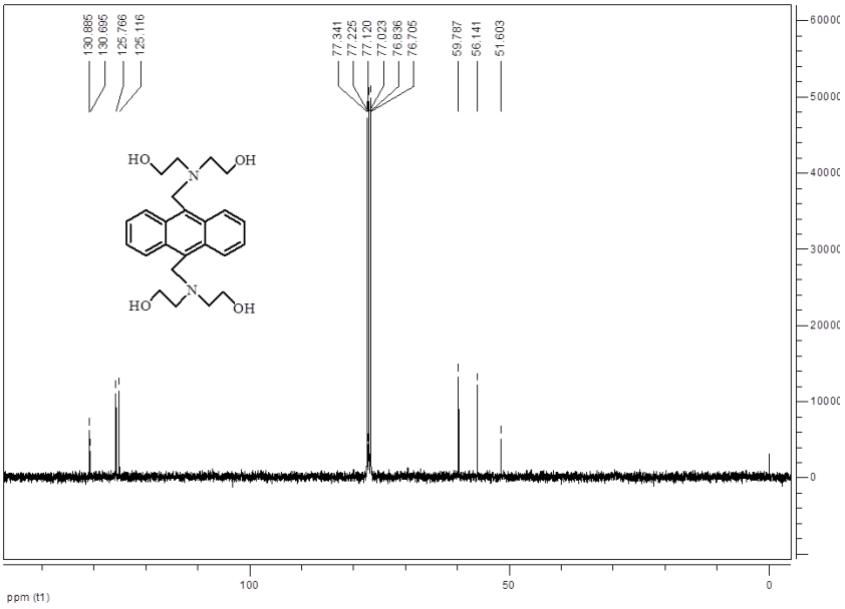

Figure S18: The ^{13}C NMR (150 MHz, $CDCl_3$) spectra of 9,10-bis[{*N*,*N*-di(2-hydroxyethyl)amino}methyl]anthracene.

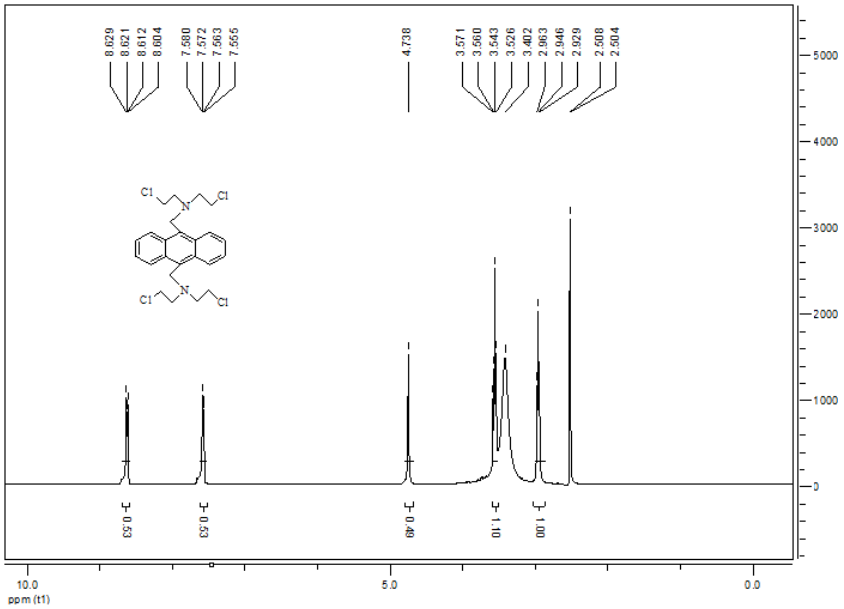

Figure S19: The ^{1}H NMR (600 MHz, DMSO-d_6) spectra of 9,10-bis[{*N*,*N*-di(2-chloroethyl)amino}methyl]anthracene.

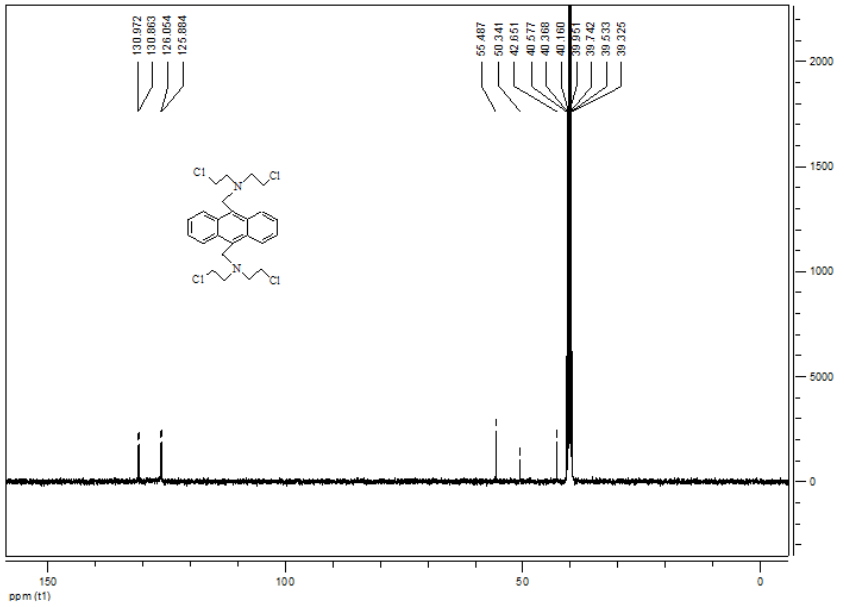

Figure S20: The ^{13}C NMR (150 MHz, DMSO-d_6) spectra of 9,10-bis[{*N*,*N*-di(2-chloroethyl)amino}methyl]anthracene.

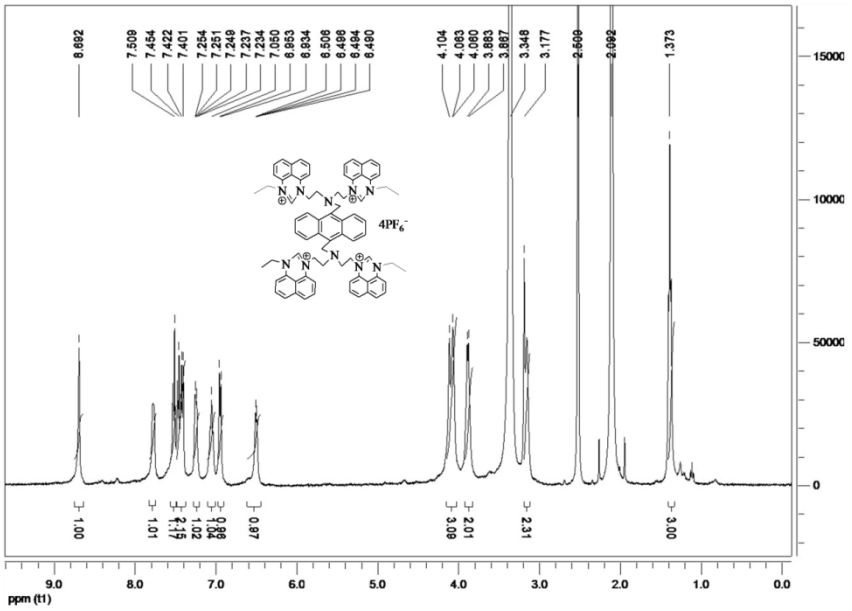

Figure S21: The ^{1}H NMR (600 MHz, DMSO-d_6) spectrum of **3.**

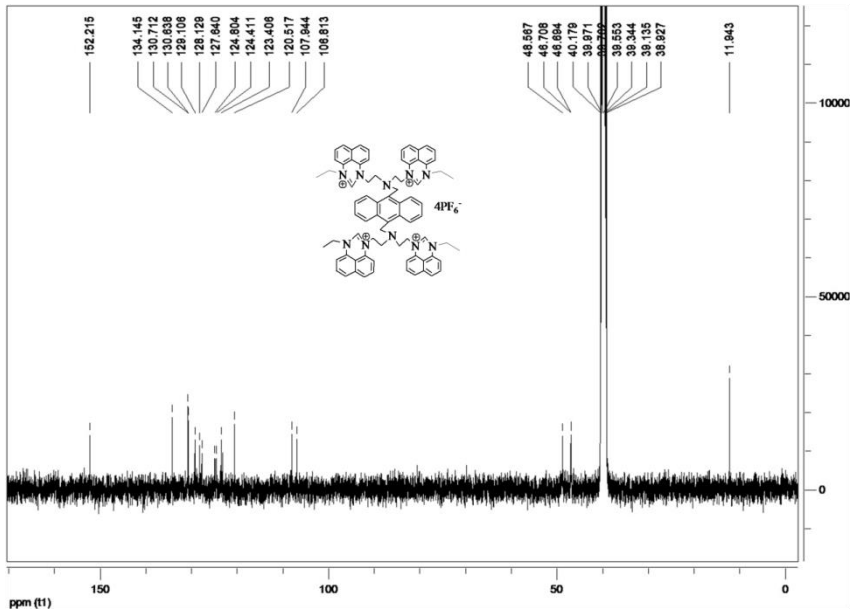

Figure S22: The ^{13}C NMR (150 MHz, DMSO-d_6) spectrum of **3**.