Electronic Supplementary Information

2,3-ethylene-bridged Dihomooxacalix[4]arenes: synthesis, X-ray crystal structures and highly selective binding properties with anions

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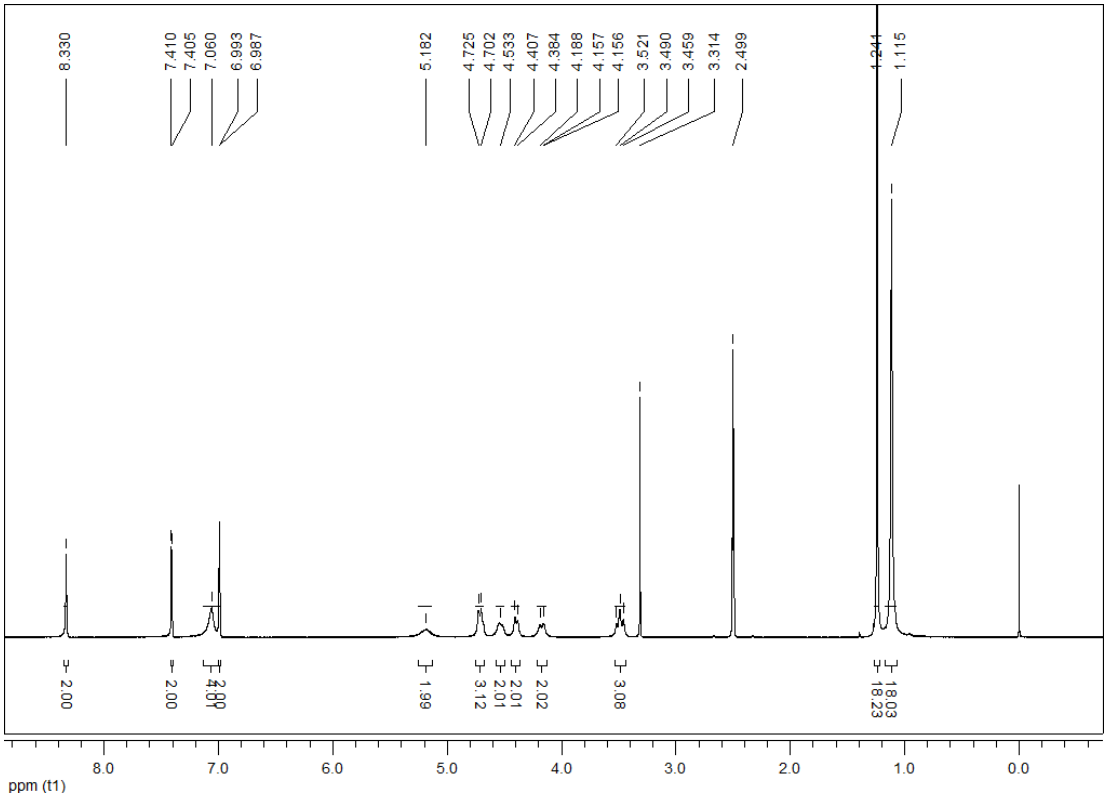
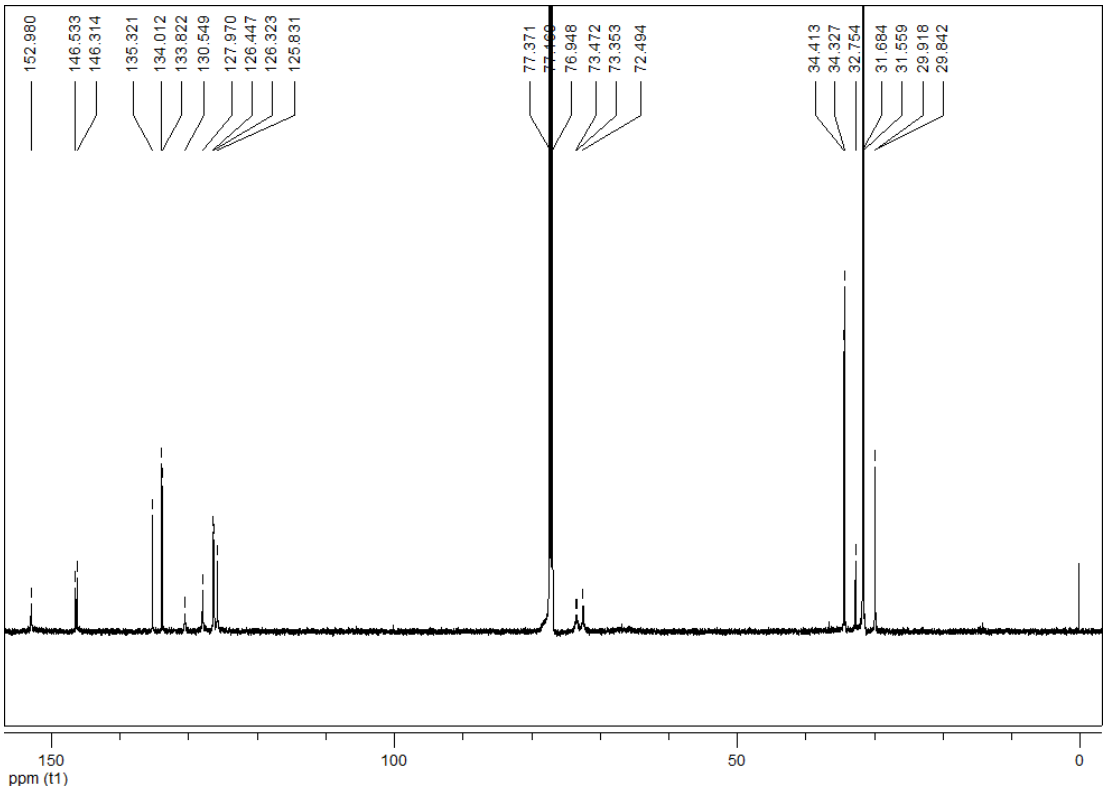
The supporting information provides the UV-Vis and fluorescent spectrum, ^{1}H NMR, ^{13}C NMR, HRMS spectra and crystal data of compounds **3a-3c** in the manuscript. All compounds were dissolved in $CDCl_3$ or DMSO-*d*6 and the ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz on a Bruker AV-400 spectrometer. HRMS data were obtained using a (UHR-TOF) maXis 4G instrument. Absorption spectra were recorded on a UV-3100 PC UV-Vis-NIR spectrophotometer. The Fluorescence data was determined by the Fluorescence spectroscopy measurements performed on an F-4600 spectrophotometer (Varian) equipped with a xenon discharge lamp using a1cm quartz cell.The single crystal of **3a-3c** were determined on Bruker Smart Apex X-single crystal diffractometer and were refined by full-matrix least- squares on F2 with SHELXS-97.

^{1}H NMR, ^{13}C NMR and HRMS spectra of 3a

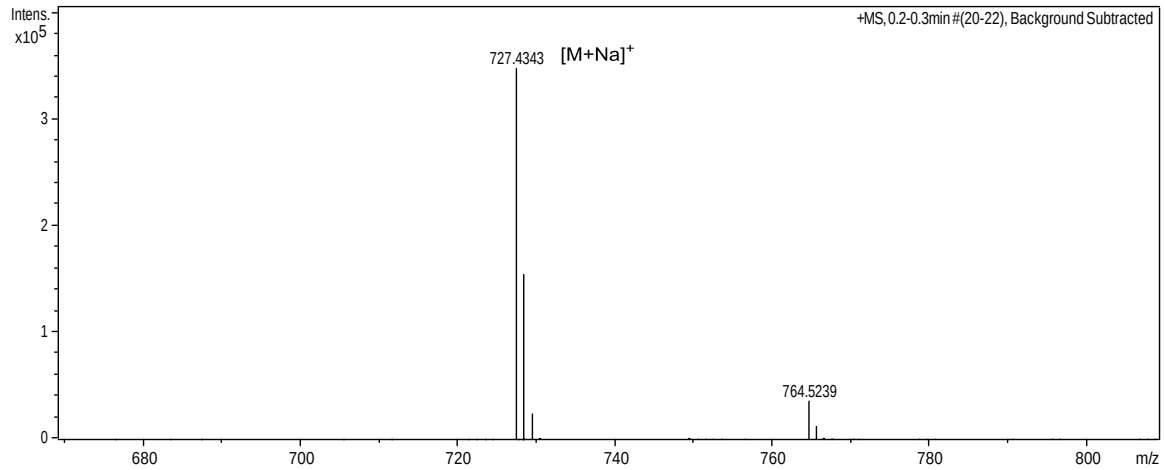
^{1}H NMR (400MHz, DMSO-d_6)



^{13}C NMR (100MHz, $CDCl_3$)

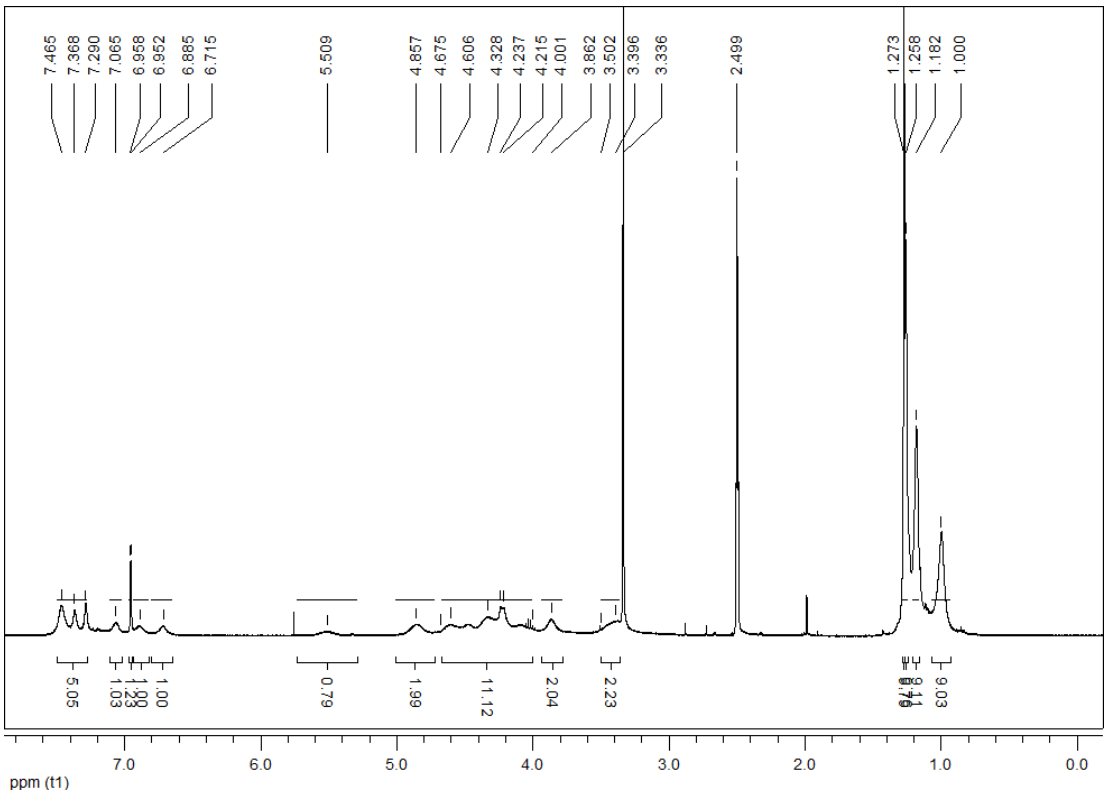


HRMS

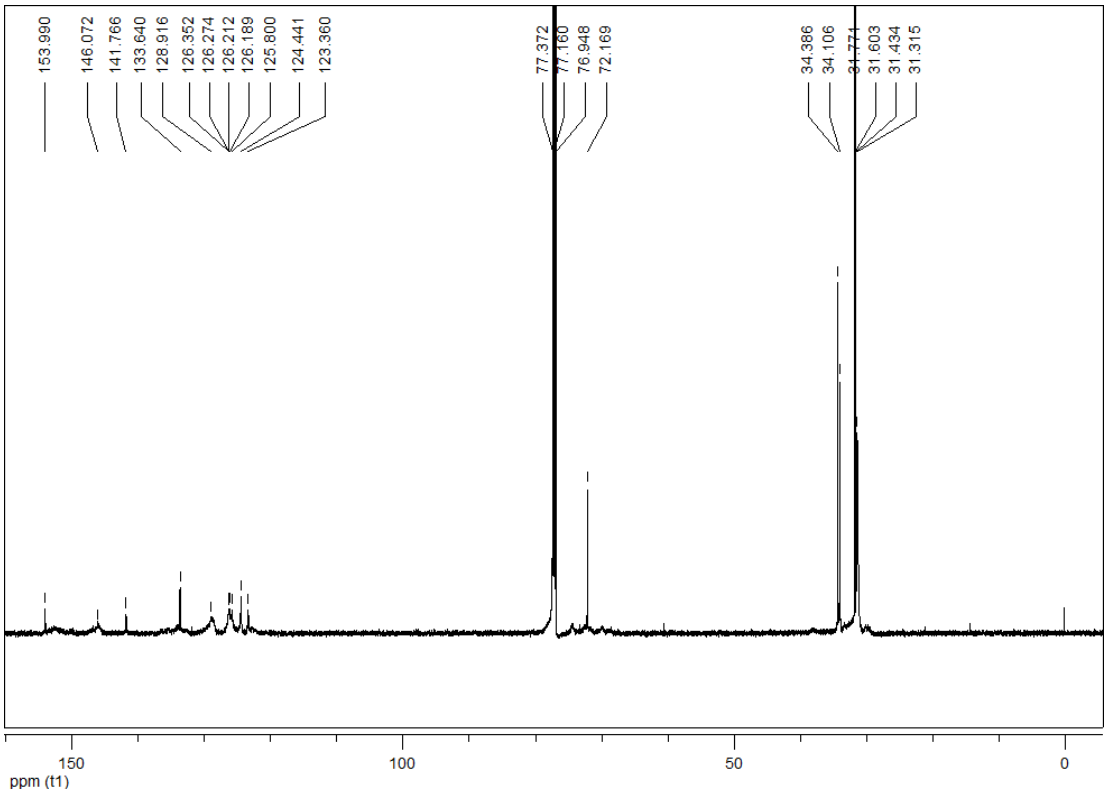


^{1}H NMR, ^{13}C NMR and HRMS spectra of 3b

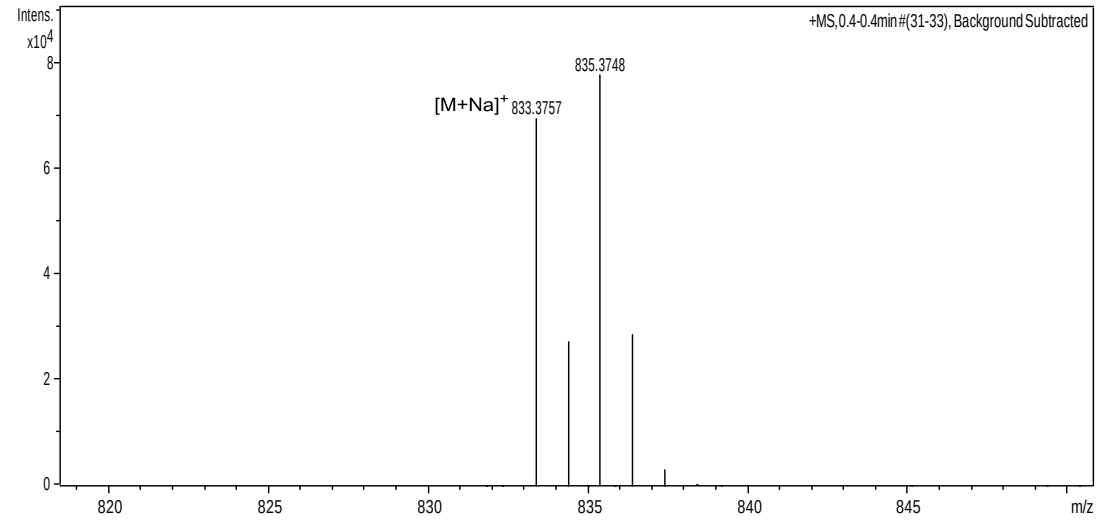
^{1}H NMR (400MHz, DMSO-d_6)



^{13}C NMR (100MHz,$CDCl_3$)

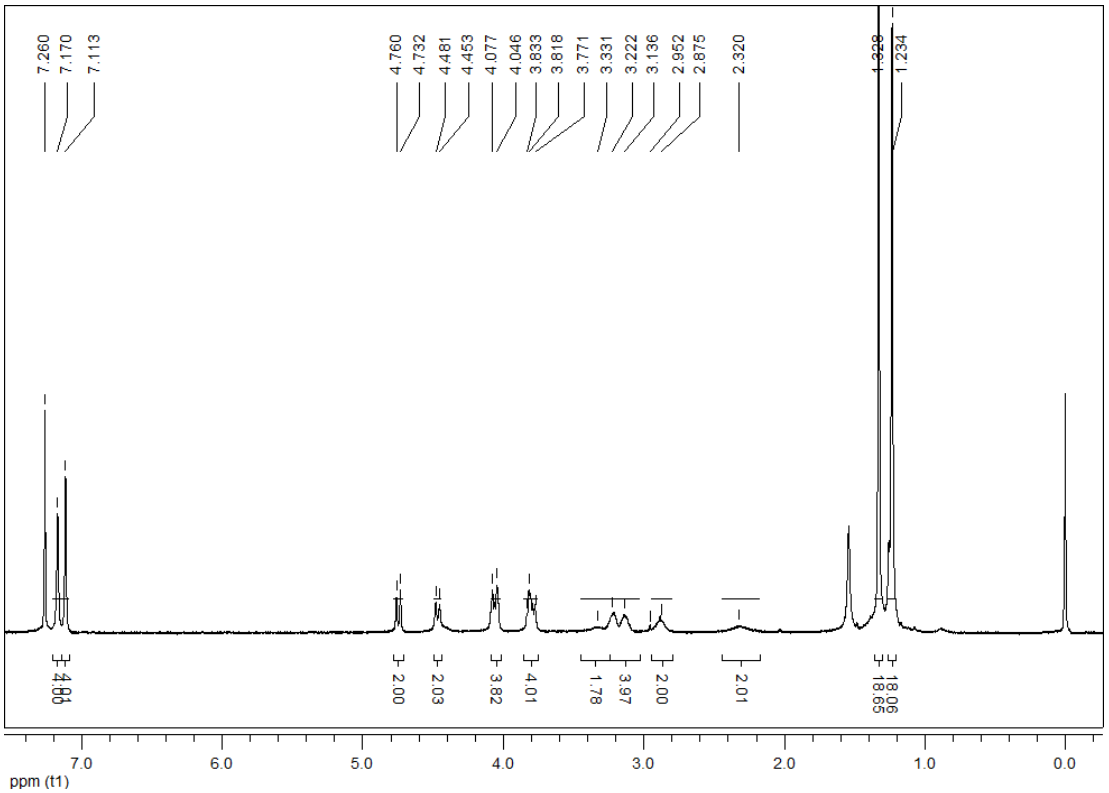


HRMS

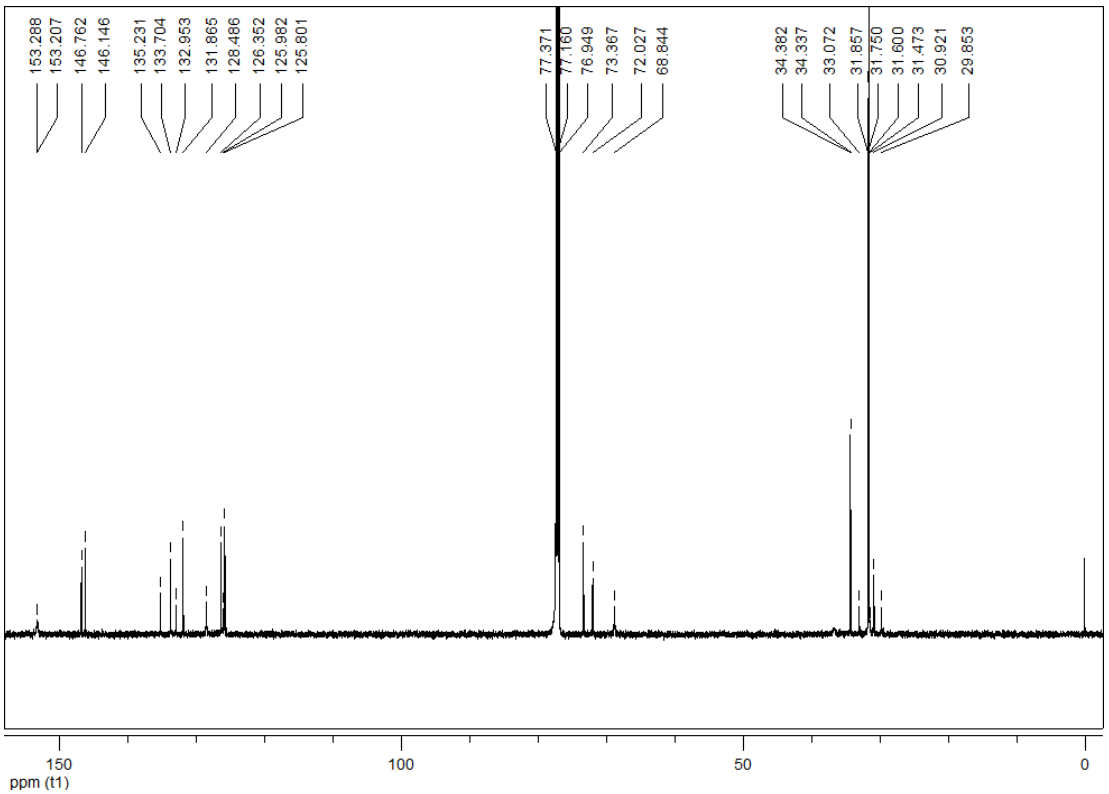


^{1}H NMR, ^{13}C NMR and HRMS spectra of compound 3c

^{1}H NMR (400MHz, $CDCl_3$)



^{13}C NMR (100MHz, $CDCl_3$)



HRMS

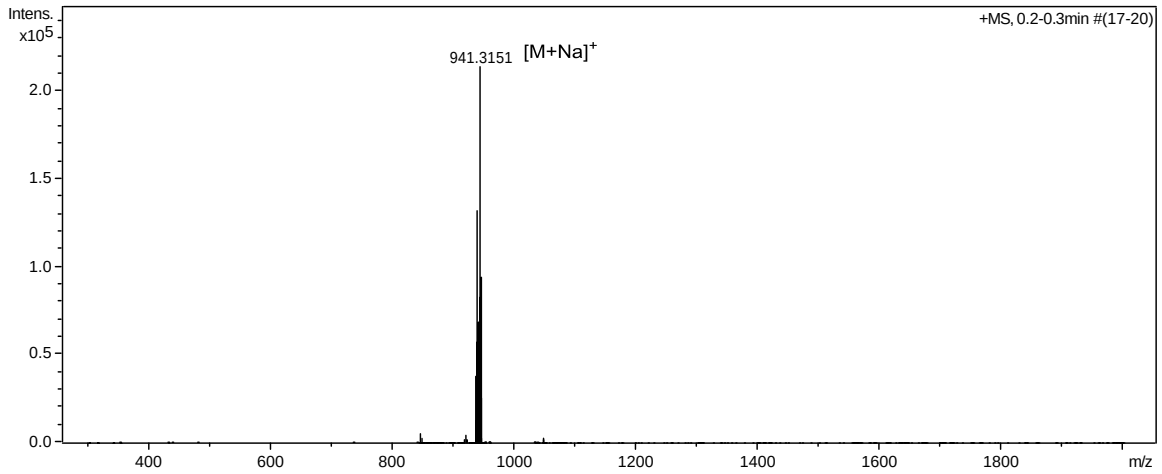


Table S1 the crystal data of 3a

Compound	**3a**
Empirical Formula	$C_{47}H_{60}O_5$
Formula weight	704.95
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, C2/c
a (Å)	32.262(4)
b (Å)	14.764(2)
c (Å)	19.644(3)
α (deg)	90
β (deg)	114.967(4)
γ (deg)	90
V (Å^3)	8483(2)
Z, Calculated density (Mg/m^3)	8, 1.104
Absorption coefficient (mm^{-1})	0.070
F(000)	3056
Crystal size (mm)	0.26 x 0.24 x 0.22
Theta range for data collection (deg)	1.739 to 27.598
Limiting indices	-39<=h<=42, -19<=k<=19, -25<=l<=25
Reflections collected / unique	32930 / 9717 [R(int) = 0.0864]
Completeness to theta = 25.00	98.9%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.985 and 0.982

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9717 / 24 / 515
GOF on F^2	1.056
Final R indices [I>2sigma(I)] R_1 [$I>2\sigma(I)$]	R1 = 0.1678, wR2 = 0.3999
R indices (all data)	R1 = 0.1994, wR2 = 0.4145
Largest diff. peak and hole (e/ Å^3)	0.837, -0.792

Table S2 The crystal data of 3b

Compound	**3b**
Empirical Formula	$C_{49}H_{63}BrO_5$
Formula weight	811.90
Temperature (K)	293(2)
Wavelength (Å)	0.71073
jCrystal system, space group	P -1,Triclinic
a (Å)	11.294(3)
b (Å)	13.330(3)
c (Å)	15.319(4)
α (deg)	80.401(7)
β (deg)	89.620(9)
γ (deg)	82.038(9)
V (Å^3)	2251.7(10)
Z, Calculated density (Mg/m^3)	2, 1.197
Absorption coefficient (mm^{-1})	0.956
F(000)	864
Crystal size (mm)	0.38 x 0.34 x 0.32
Theta range for data collection (deg)	1.821 to 24.998
Limiting indices	-13<=h<=13, -15<=k<=15, -17<=l<=18
Reflections collected / unique	25207 / 7763 [R(int) = 0.2251]
Completeness to theta = 25.00	98.0
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.736, 0.702
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7763 / 146 / 555
GOF on F^2	1.057

Final R indices [I>2sigma(I)] R_1 [$I>2\sigma(I)$]	R1 = 0.1281, wR2 = 0.2311
R indices (all data)	R1 = 0.3615, wR2 = 0.3037
Largest diff. peak and hole (e/ $Å^3$)	0.426 and -0.472

Table S3 The crystal data of 3c

Compound	**3c**
Empirical Formula	$C_{51}H_{66}Br_2O_5$
Formula weight	918.85
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system, space group	Orthorhombic, P b c n
a (Å)	27.808(3)
b (Å)	17.183(2)
c (Å)	21.075(2)
α (deg)	90
β (deg)	90
γ (deg)	90
V ($Å^3$)	10070(2)
Z, Calculated density (Mg/m^3)	8, 1.212
Absorption coefficient (mm^{-1})	1.652
F(000)	3856
Crystal size (mm)	0.26 x 0.22 x 0.20
Theta range for data collection (deg)	1.393 to 25.497
Limiting indices	-32<=h<=33, -20<=k<=18, -23<=l<=25
Reflections collected / unique	76689 / 9368[R(int) = 0.079]
Completeness to theta = 25.00	99.9%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.719 and 0.657
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9368 / 327 / 664
GOF on F^2	1.024
Final R indices [I>2sigma(I)] R_1 [$I>2\sigma(I)$]	R1 = 0.0538, wR2 = 0.1255
R indices (all data)	R1 = 0.1222, wR2 = 0.1546
Largest diff. peak and hole (e/ $Å^3$)	0.337, -0.432

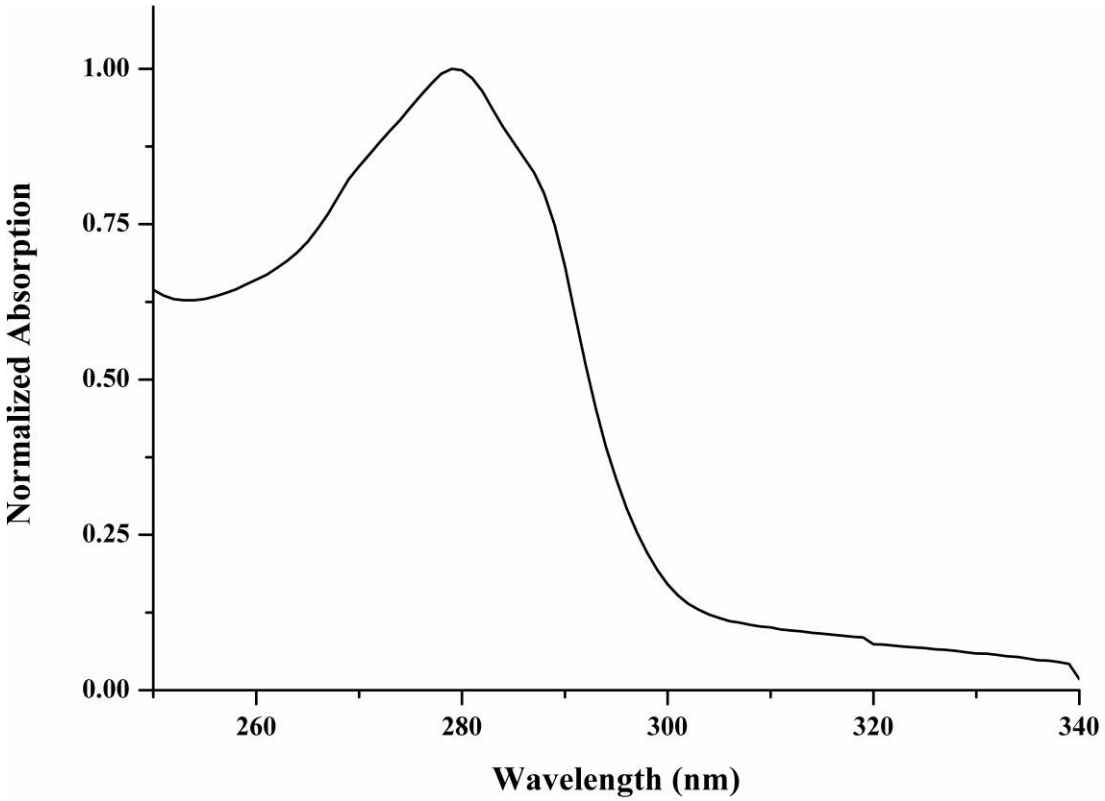


Fig. S1 Normalized absorption spectra of 3a (50 µM)

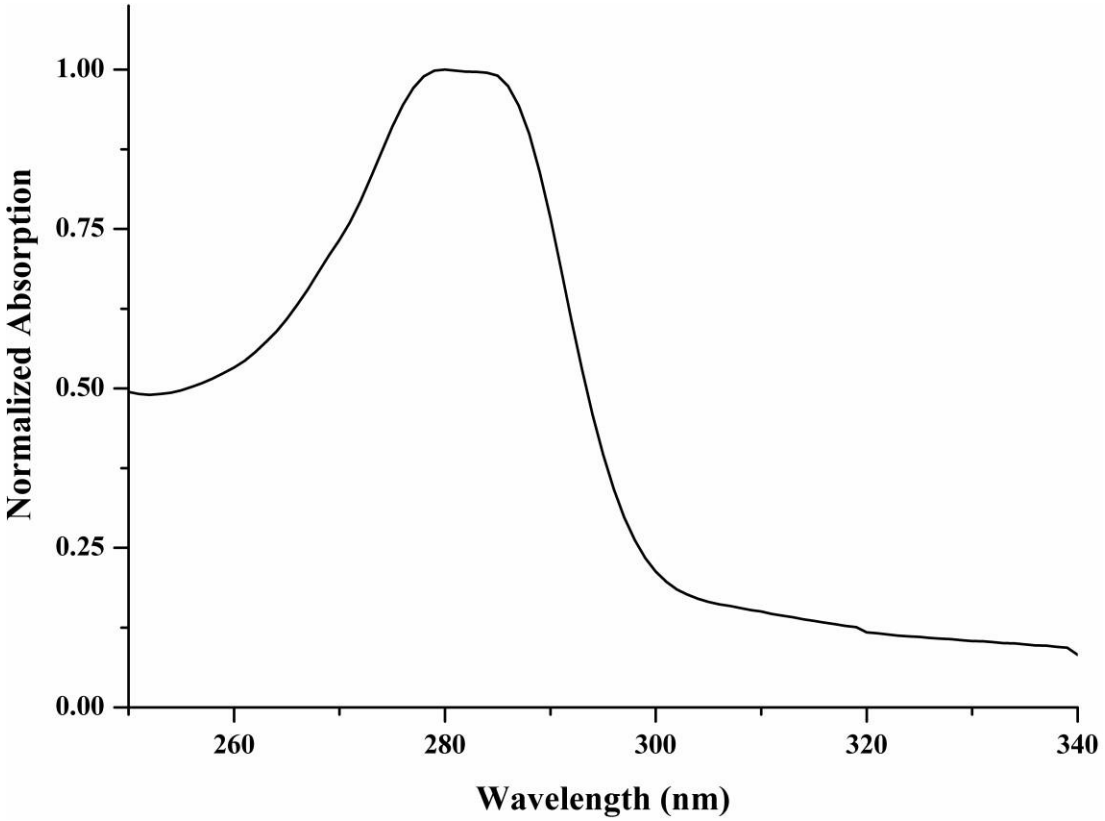


Fig. S2 Normalized absorption spectra of 1 (50 µM)

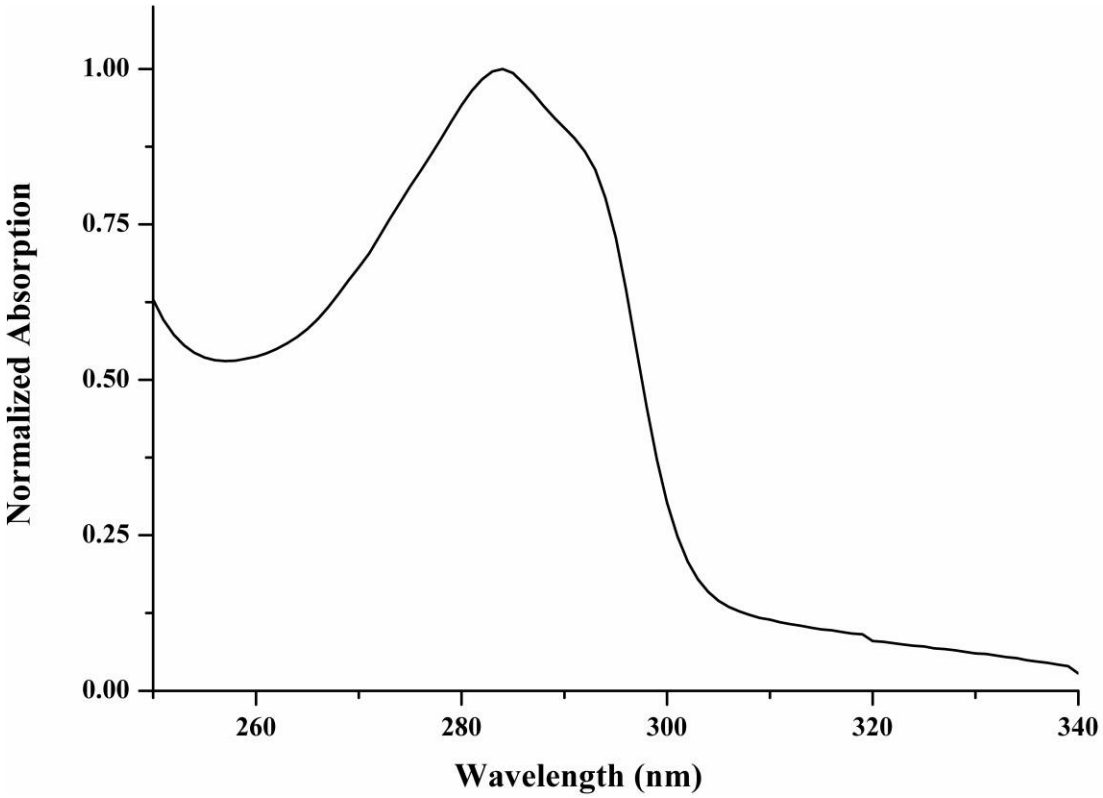


Fig. S3 Normalized absorption spectra of 4 (50 μM)

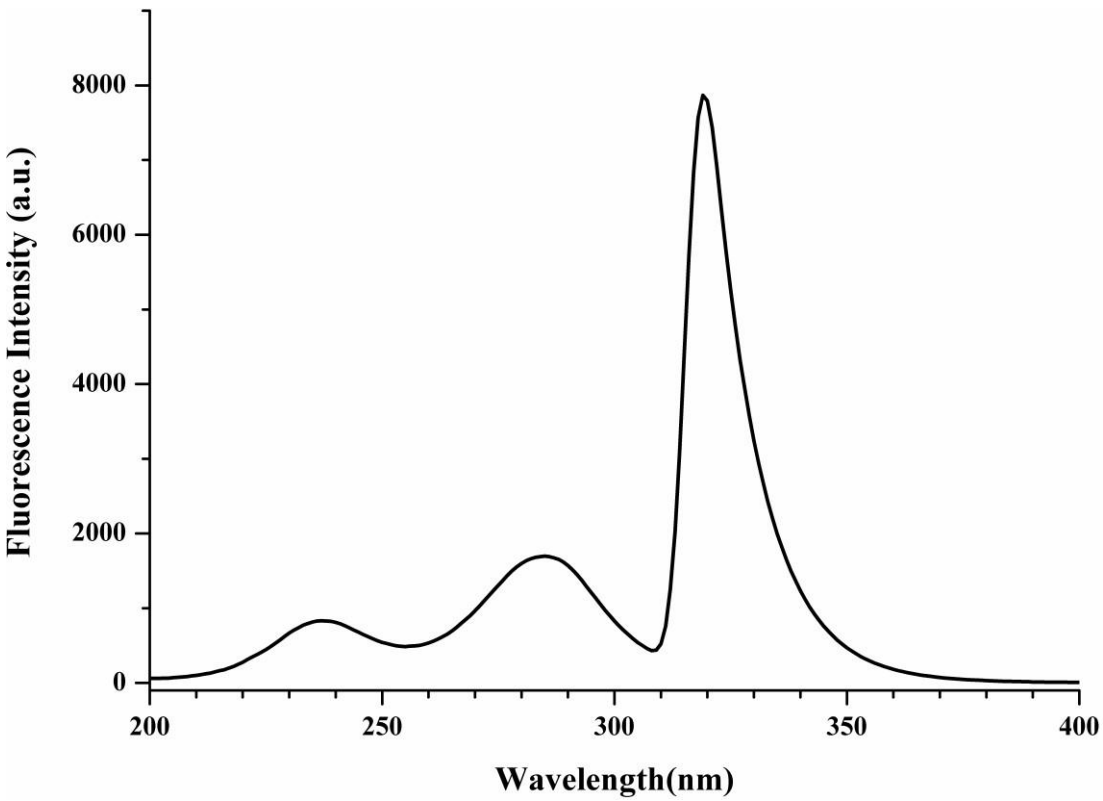


Fig. S4 The excitation spectra of 3a

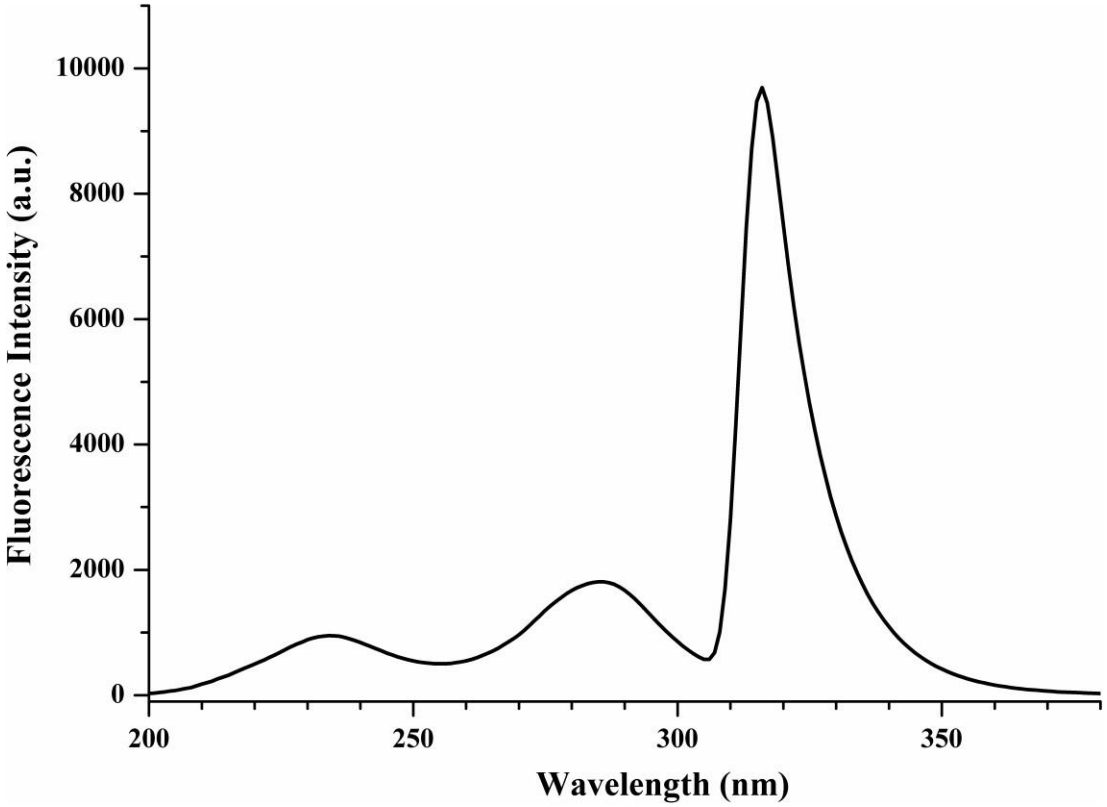


Fig. S5 The excitation spectra of 1

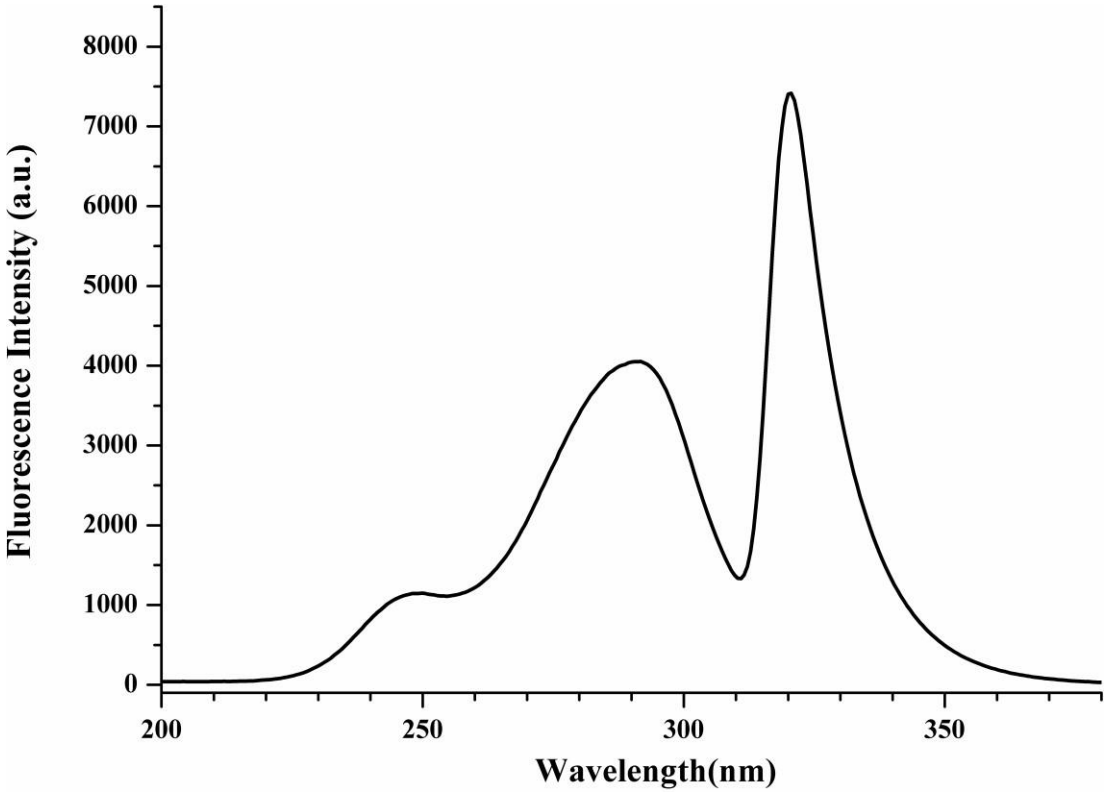


Fig. S6 The excitation spectra of 4