Supporting Information

Fluorescent phenylethynylene Calix[4]arenes for sensing TNT in aqueous media and vapor phase

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Table S1 Photophysical and HOMO, LUMO data.

Compound	Absorption		Fluorescence		HOMO	LUMO
	λ_{max} (nm)	log ε	λ_{max} (nm)	Φ (%)	(eV)	(eV)
BAC	310	4.98	433	10.0	-5.64	-2.18
SAC	314	4.98	433	5.0	-5.03	-1.56
ANC	315	5.08	421	7.0	-4.84	-1.54

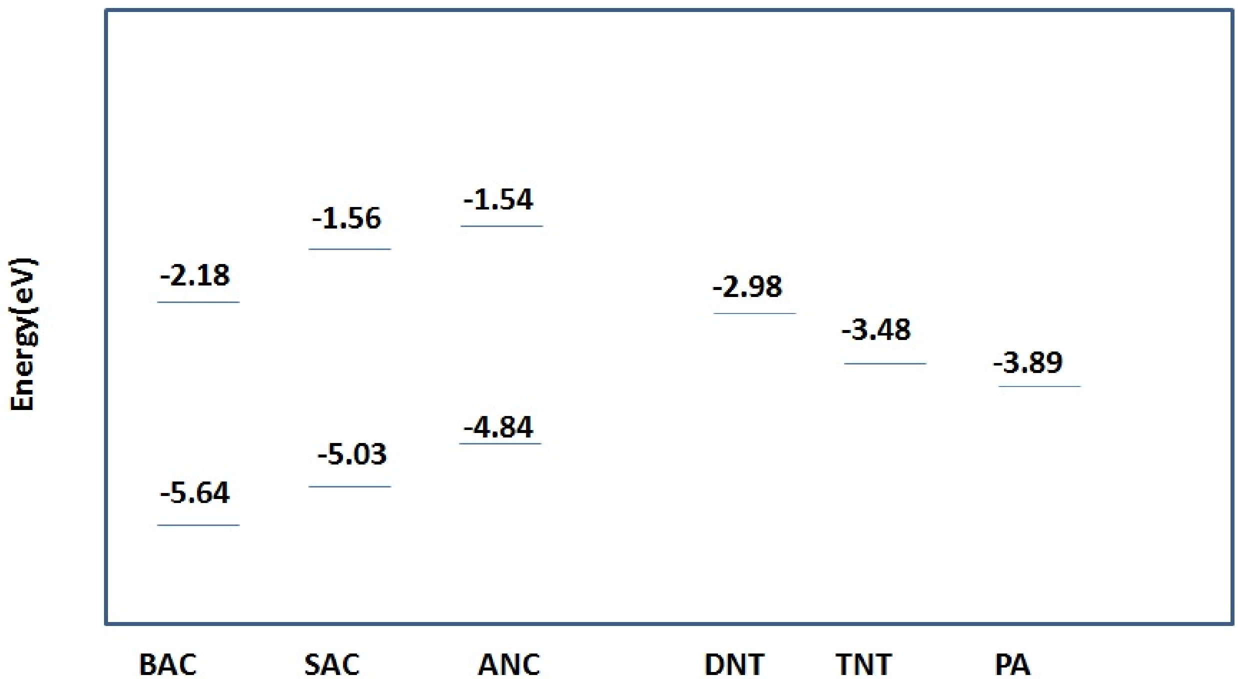

Fig S1 HOMO and LUMO energy levels calculated for **BAC**, **SAC**, **ANC**, and some explosive analytes such as DNT, TNT, and PA.

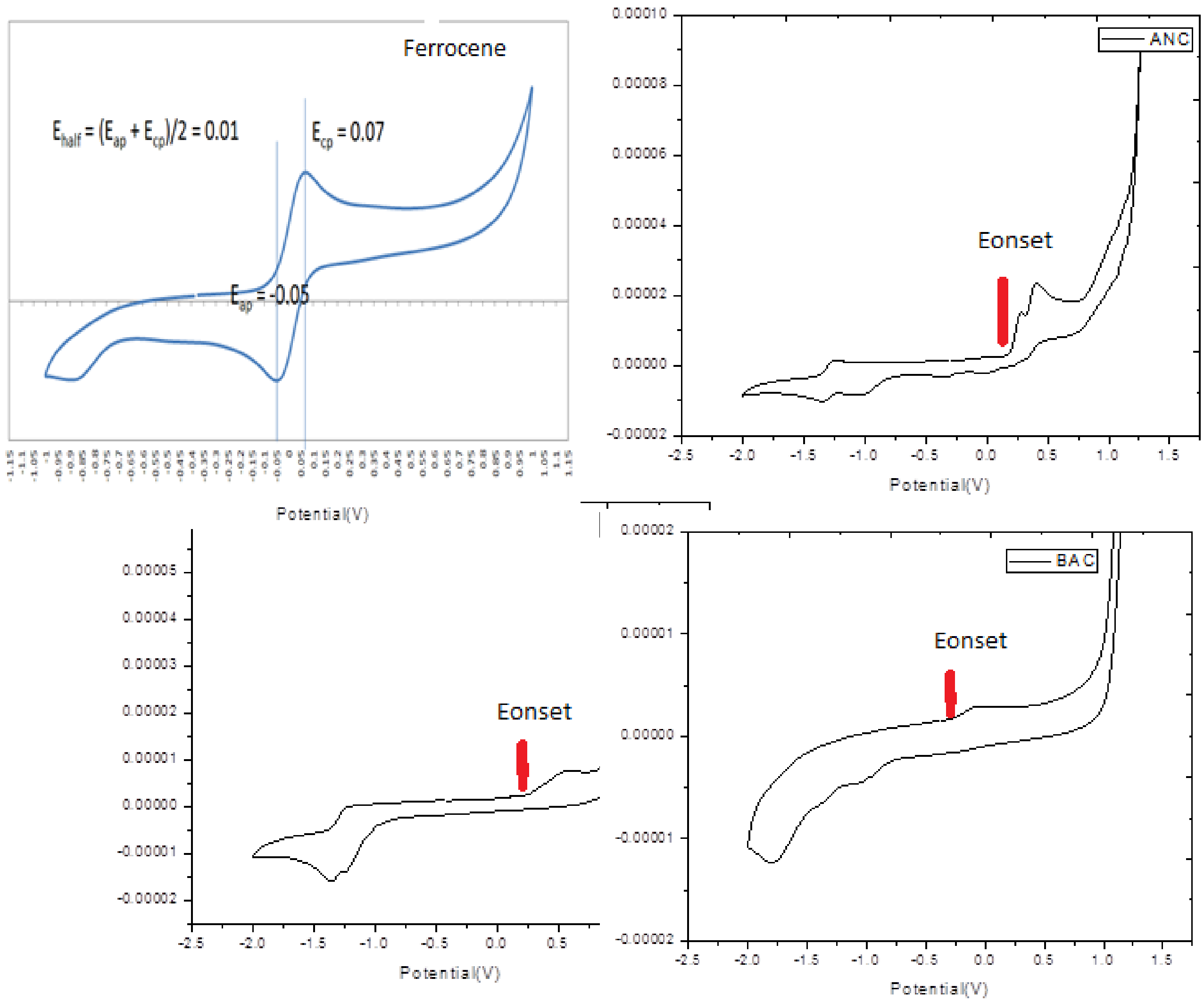

Fig. S2 Cyclic voltammogram of ferrocene, ANC, SAC, and BAC in DMF used for determination of HOMO and LUMO.

$E_{HOMO} = -(E(ox)_{onset} - E_{half} + 4.8)^{a}$

$E(ox)_{onset}$ is the onset oxidation potential

$E_{gap} = 1242/\lambda_{cut\ off}$ where $\lambda_{cut\ off}$ is the longest wavelength which give minimum absorption

$E_{LUMO} = E_{HOMO} + E_{gap}$

(a) Deng, P.; Liu, L.; Ren, S.; Li, H.; Zhang, Q. *Chem. Commun.,* **2012**, *48,* 6960.;(2) Tsai, J.-H.; Lee, W.-Y.; Chen, W.-C.; Yu, C.-Y.; Hwang, G.-W.; Ting, C. *Chem. Mater*., **2010**, *22*, 3290; (c) Lu, C.; Wu, H. C.; Chiu, Y. C.; Lee, W. Y.; Chen, W. C. *Macromolecules*, **2012**, *45*, 3047.

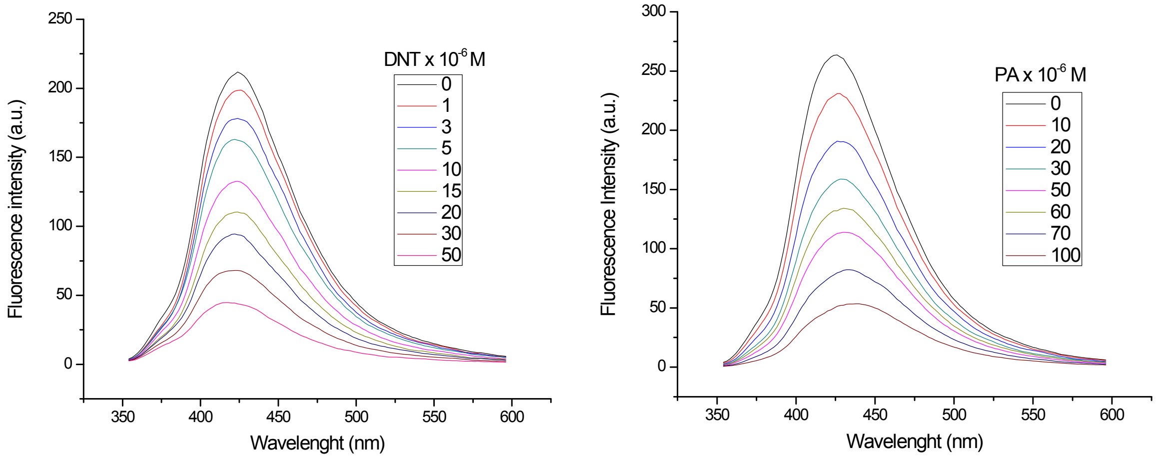

Fig. S3 Fluorescence responses of ANC to DNT and PA.

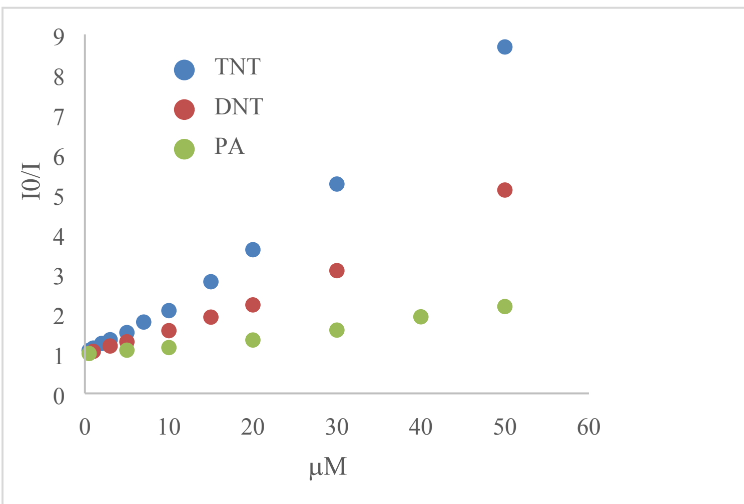

Fig. S4 Stern-Volmer plots for fluorescence quenching of ANC with TNT, DNT and PA.

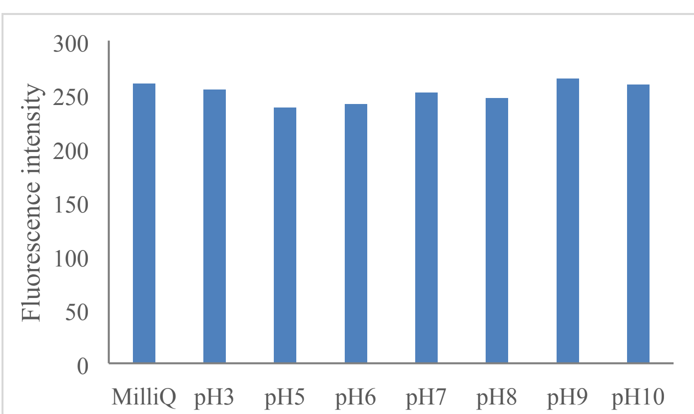

Fig. S5 Fluorescence intensity of ANC 0.5 µM at λ_{max} = 420 nm in various pH.

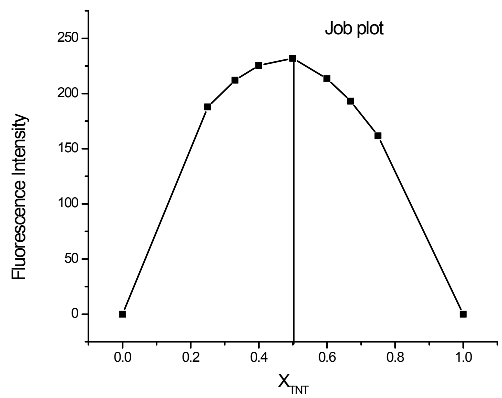

Fig. S6 Job's plot of fluorescence responses of **ANC** upon addition of TNT showing 1:1 stoichiometry.

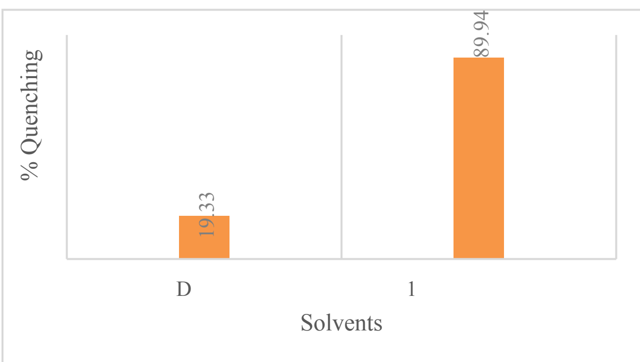

Fig. S7 Fluorescence quenching of ANC for TNT 100 equiv in DMF and 1%THF/H_2O.

Fig. S8 Impression of a glove-wearing thumb after rubbing with various nitroaromatic compounds.

Table S2 Fluorescence quenching effects of TNT and PA found in this work in comparison with previously reported literature works

TNT		PA		Media	References
K_{sv} (M^{-1})	%Q at 10 µM	K_{sv} (M^{-1})	%Q at 10 µM		
$3.65x10^4$	-	$4.5x10^2$	-	Film in aqueous	*b*
$1.2x10^5$	-	$1.8x10^3$	-	Film in aqueous	*c*
$1.33x10^6$	94%	-	20%	AIE in 20%THF/H_2O	*d*
$1.45x10^5$	-	$1.2x10^4$	-	Film in aqueous	*e*
$1.37x10^5$	-	-	-	AIE 5% THF/H_2O	*f*
$9.48x10^4$	-	$1.84 x10^4$ -	-	Fe_3O_4@Tb-BTC nanospheres in EtOH	*g*
-	95%	-	55%	Film in aqueous	*h*
$1.09x10^5$	52%	$2.1x10^4$	13%	in aqueous	This work

(b) He, G.; Yan, N.; Yang, J.; Wang, H.; Ding, L.; Yin, S.; Fang, Y. *Macromolecules*, **2011**, *44*, 4759.
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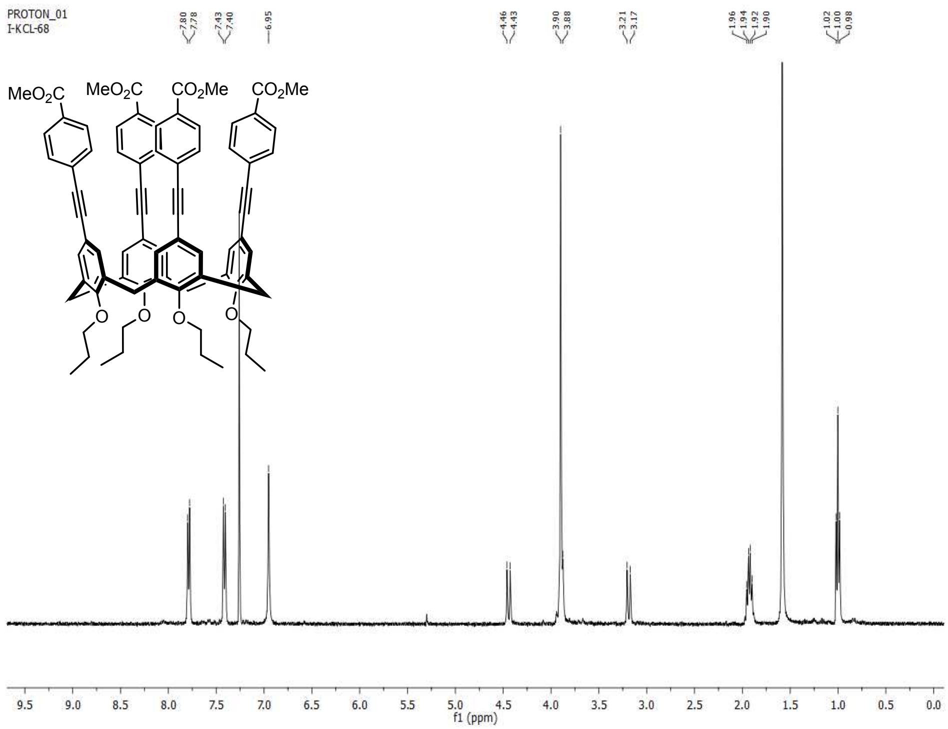
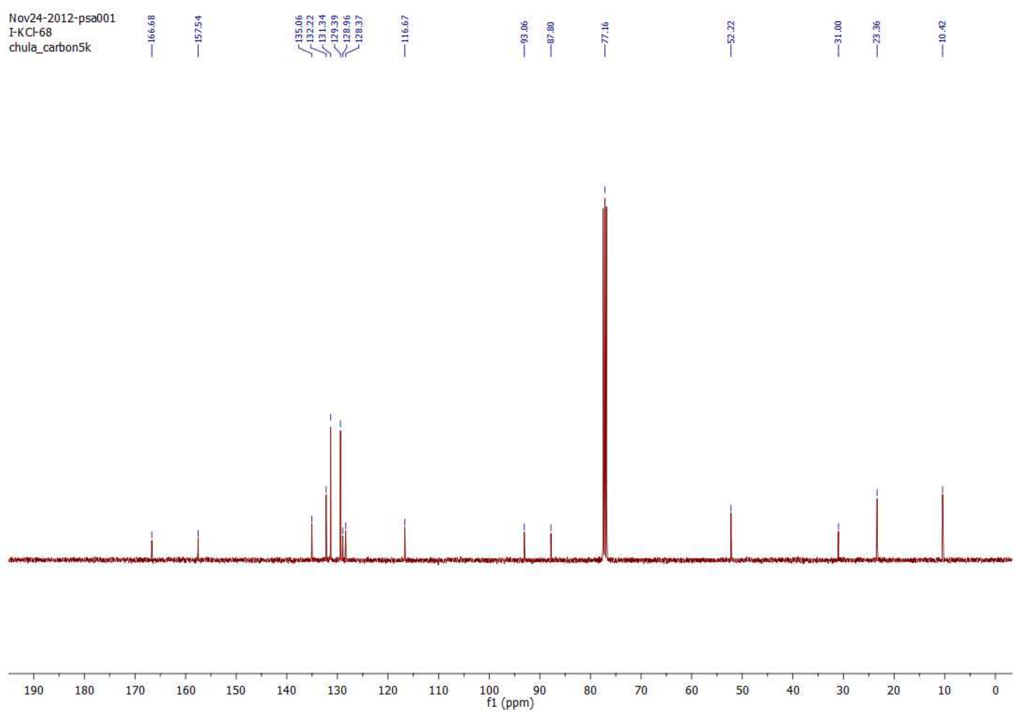
(e) Jagtap, S. B.; Potphode, D. D.; Ghorpade, T. K.; Palai, A. K.; Patri, M.; Mishra, S. P. *Polymer,* **2014**, *55*, 2792.
(f) Feng, H. T.; Wang, J. H.; Zheng, Y. S. *ACS Appl. Mater. Interfaces*, dx.doi.org/10.1021/am505636f
(g) Qian, J. J.; Qiu, L. G.; Wang, Y. M.; Yuan, Y. P.; Xie, A. J.; Shen, Y. H. *Dalton Trans*., **2014**, *43*, 3978.
(h) Kartha, K. K.; Sandeep, A.; Nair, V. C.; Takeuchi, M.; Ajayaghosh, A. *Phys. Chem. Chem. Phys.,* **2014**, *16,* 18896.

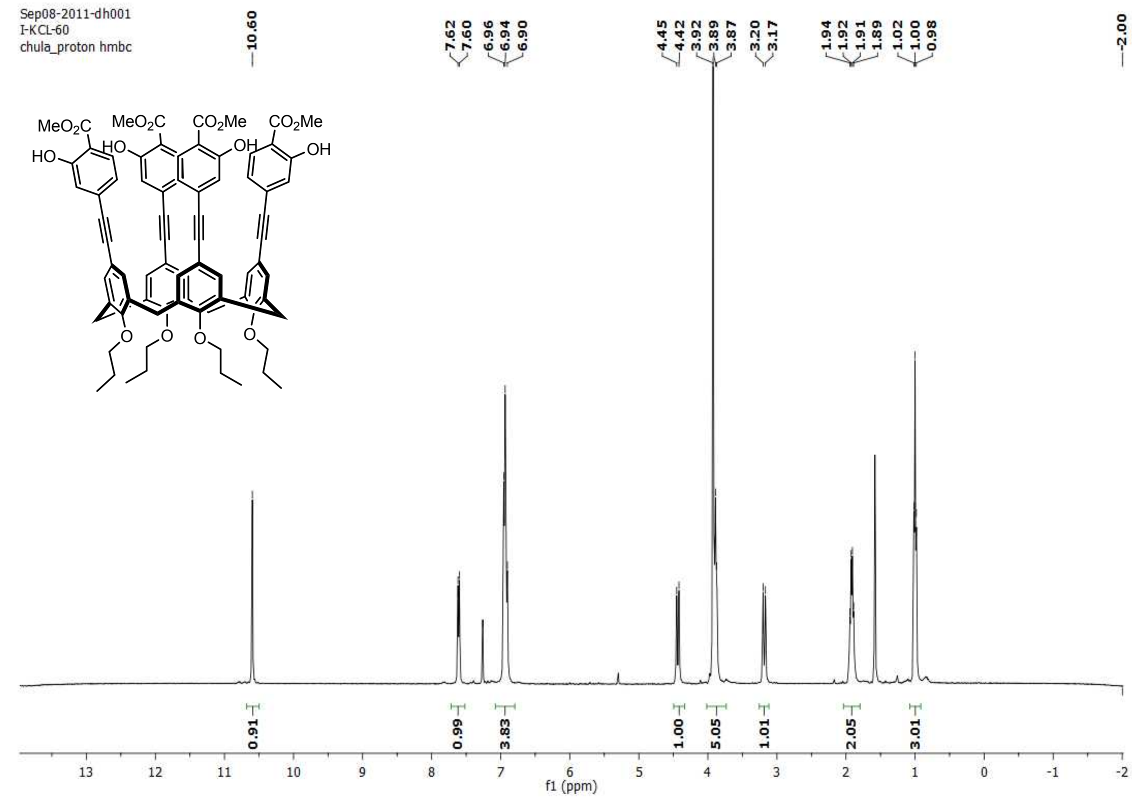
H[1]-NMR (400 MHz) of **2a** in $CDCl_3$



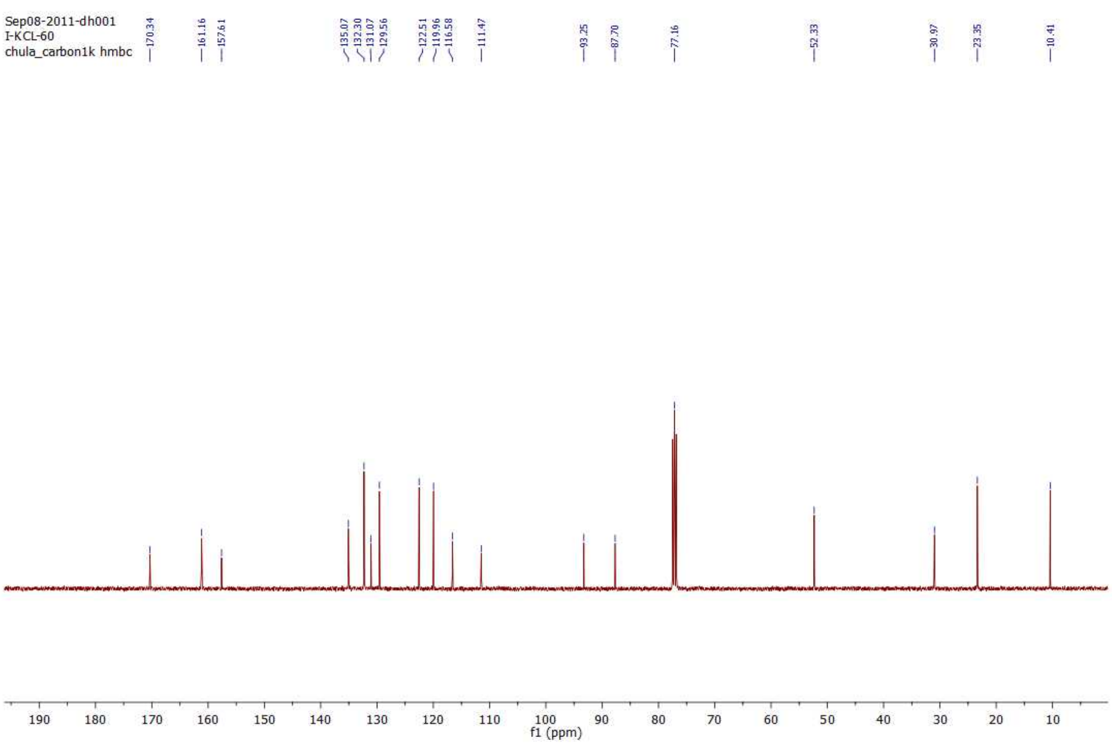
C[13]-NMR (100 MHz) of **2a** in $CDCl_3$



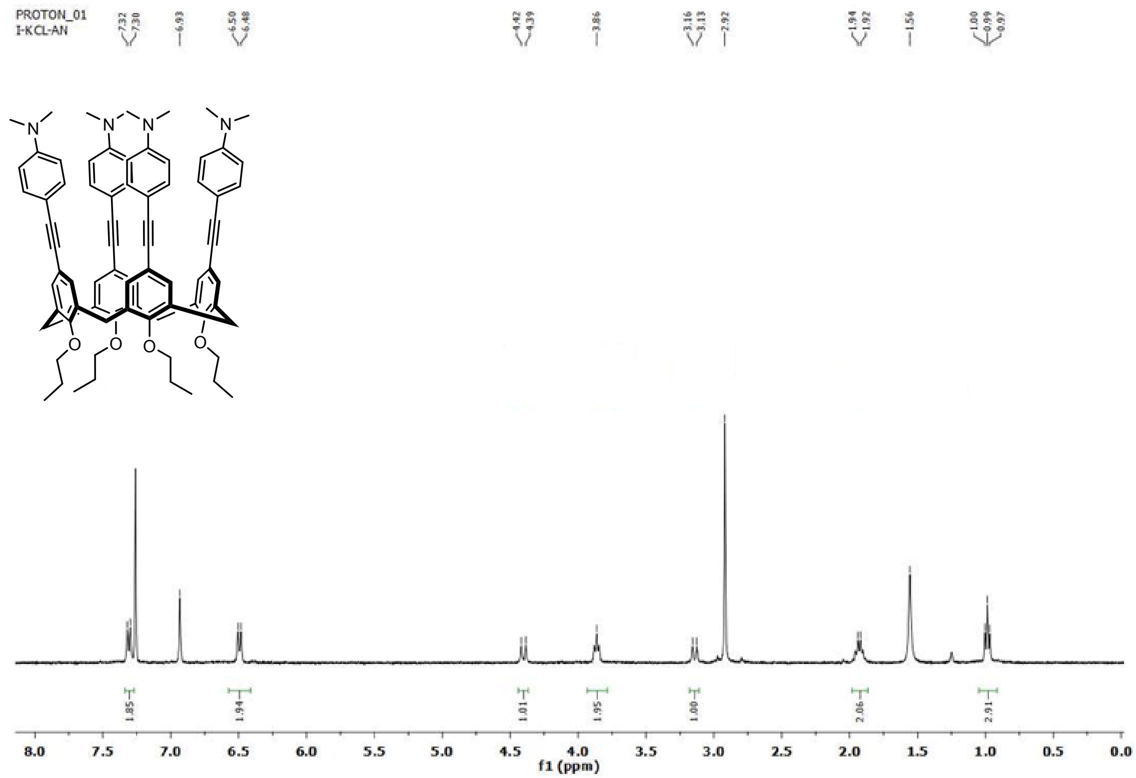
H[1]-NMR (400 MHz) of **2b** in $CDCl_3$



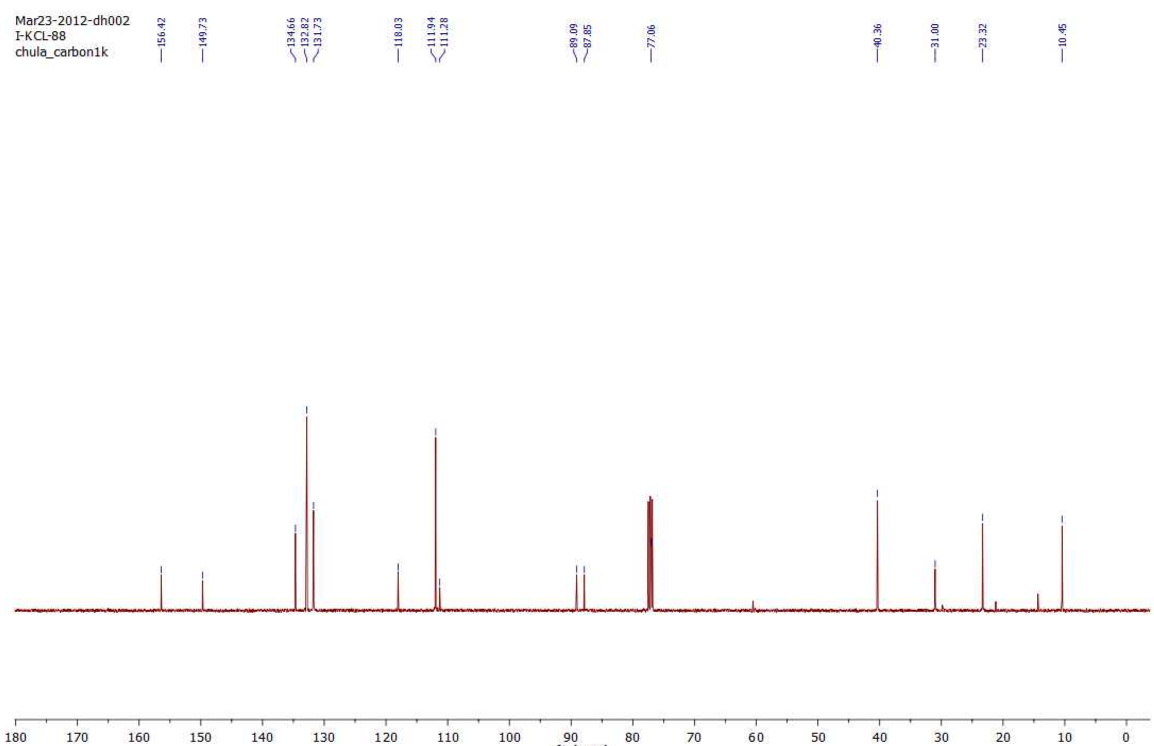
C[13]-NMR (100 MHz) of **2b** in $CDCl_3$



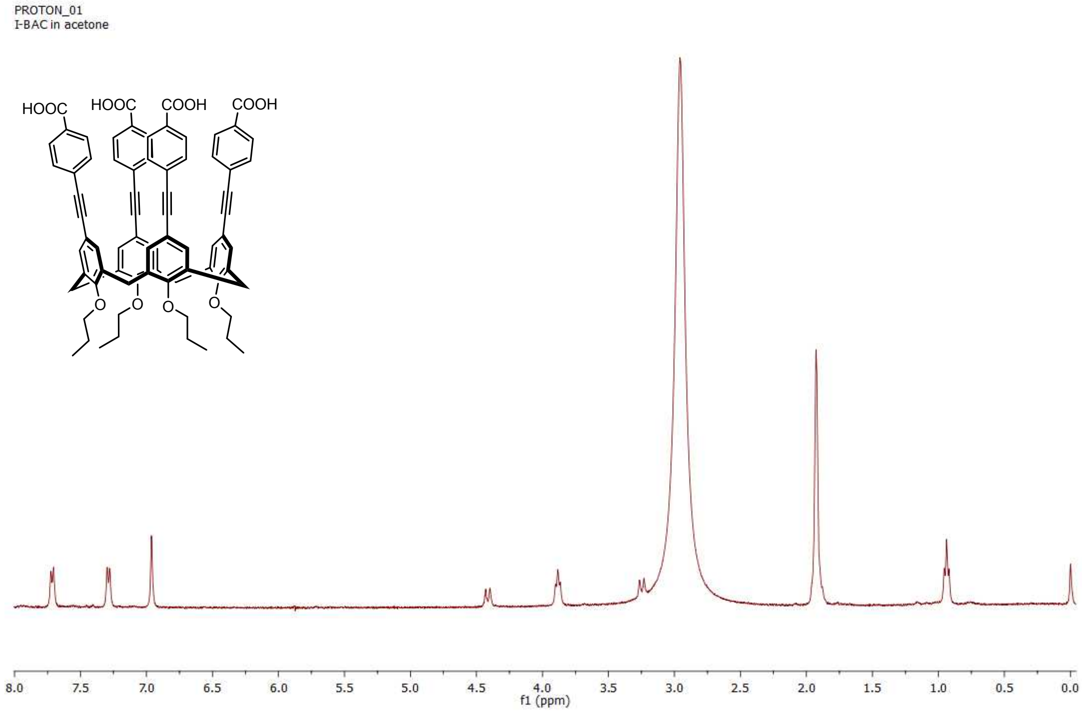
H[1]-NMR (400 MHz) of **ANC** in $CDCl_3$



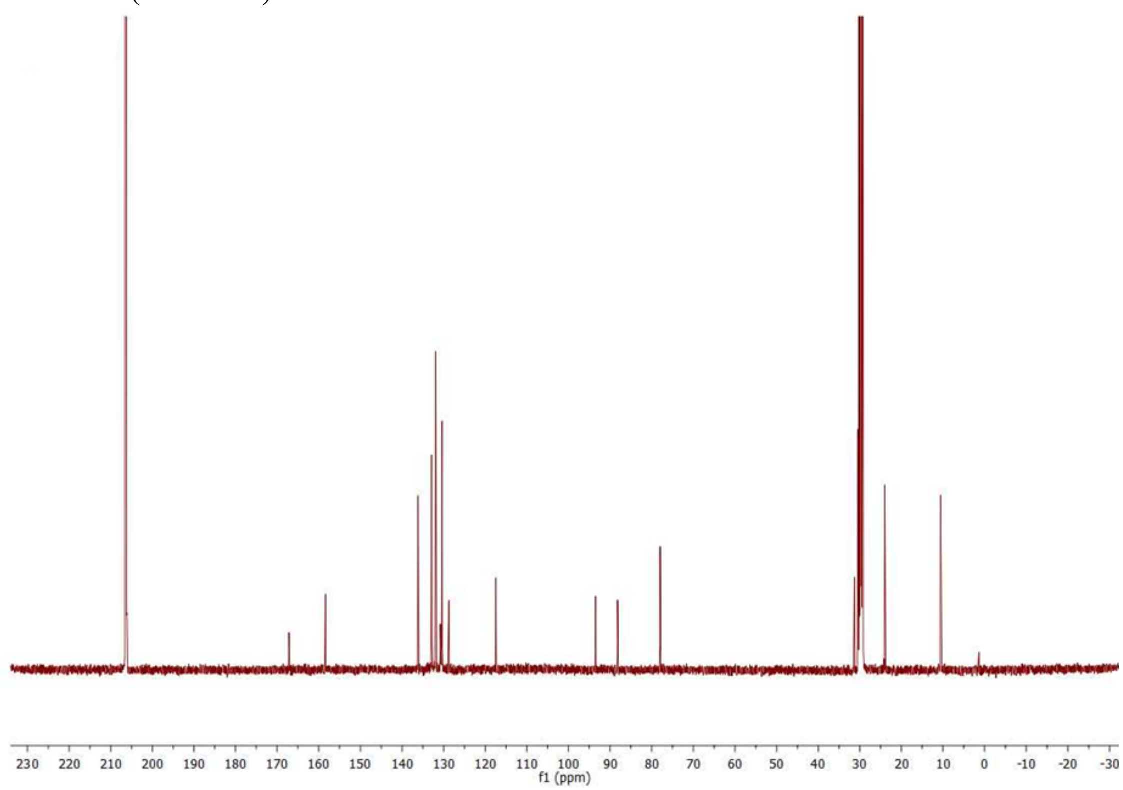
C[13]-NMR (100 MHz) of **ANC** in $CDCl_3$



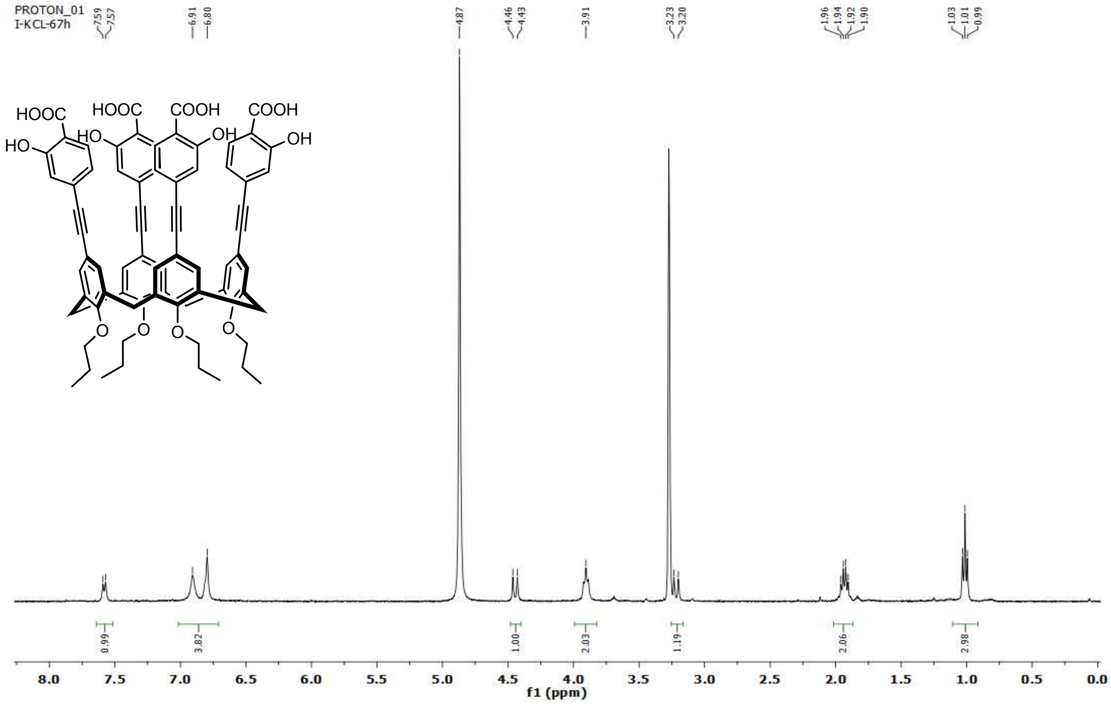
H^1-NMR (400 MHz) of **BAC** in Acetone-d6



C^{13}-NMR (100 MHz) of **BAC** in Acetone-d6



H[1]-NMR (400 MHz) of **SAC** in Metanol-d4



C[13]-NMR (100 MHz) of **SAC** in Metanol-d4