Supporting Information

The Sensitive and Efficient Trifluoroacetyl-based Aromatic Fluorescent Probe for Organic Amine Vapour Detection

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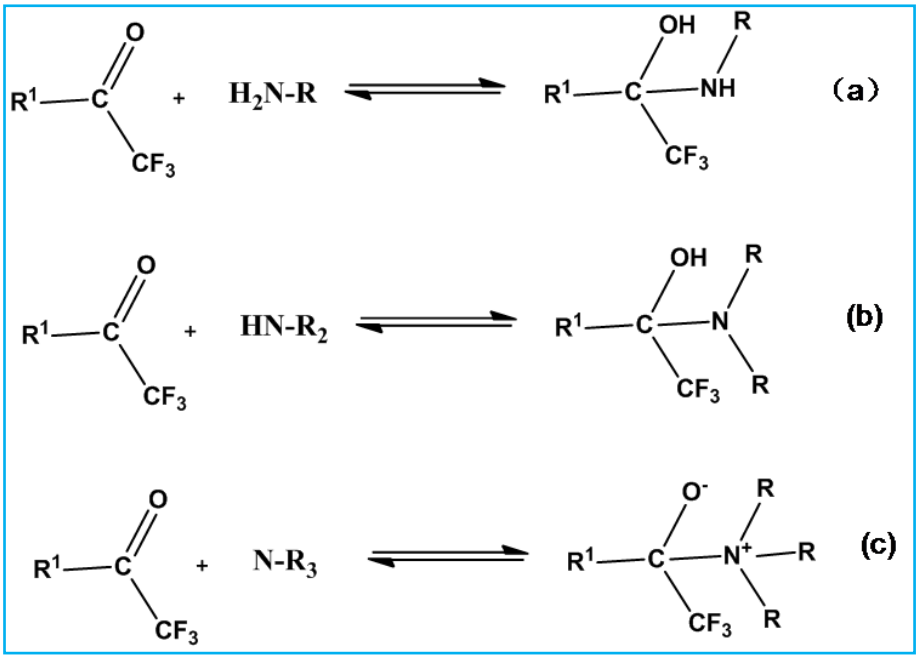

Figure S1. Chemical reaction of trifluoroacetyl group with primary (a) and secondary (b) tertiary (c) amines.

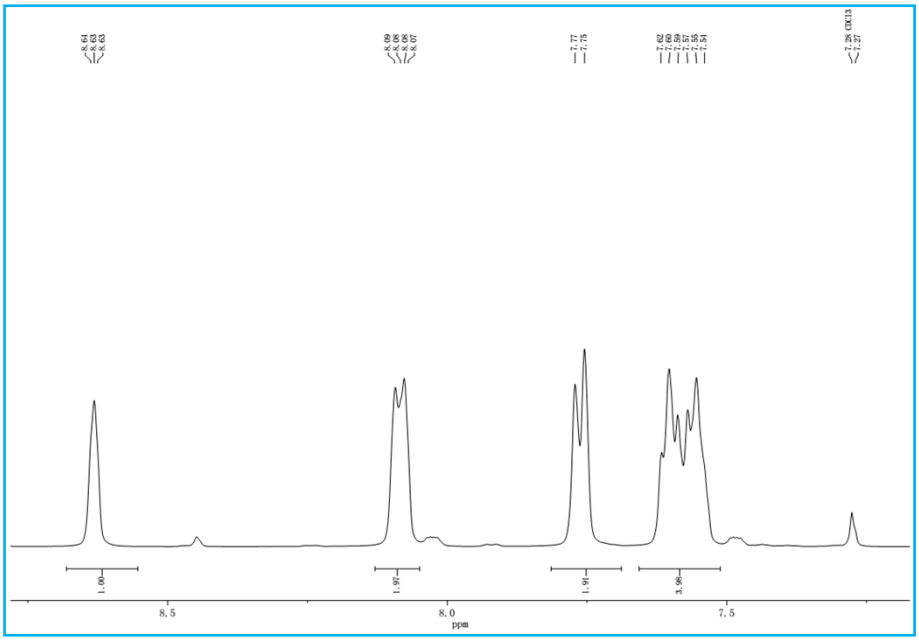

Figure S2. ^{1}H NMR spectrum of **ANT-TFA** in $CDCl_3$.

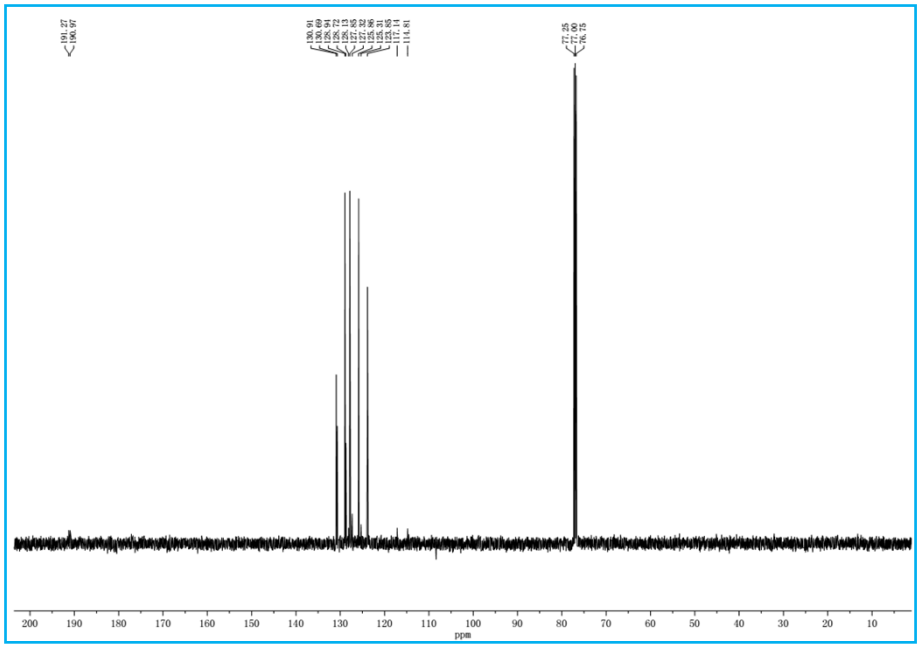

Figure S3. ^{13}C NMR spectrum of **ANT-TFA** in $CDCl_3$.

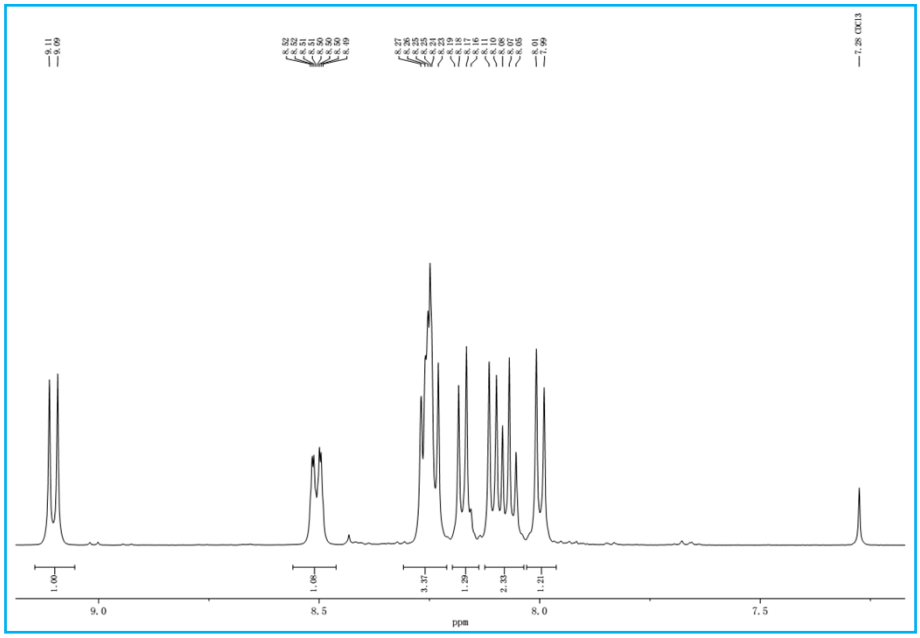

Figure S4. ^{1}H NMR spectrum of **PY-TFA** in $CDCl_3$.

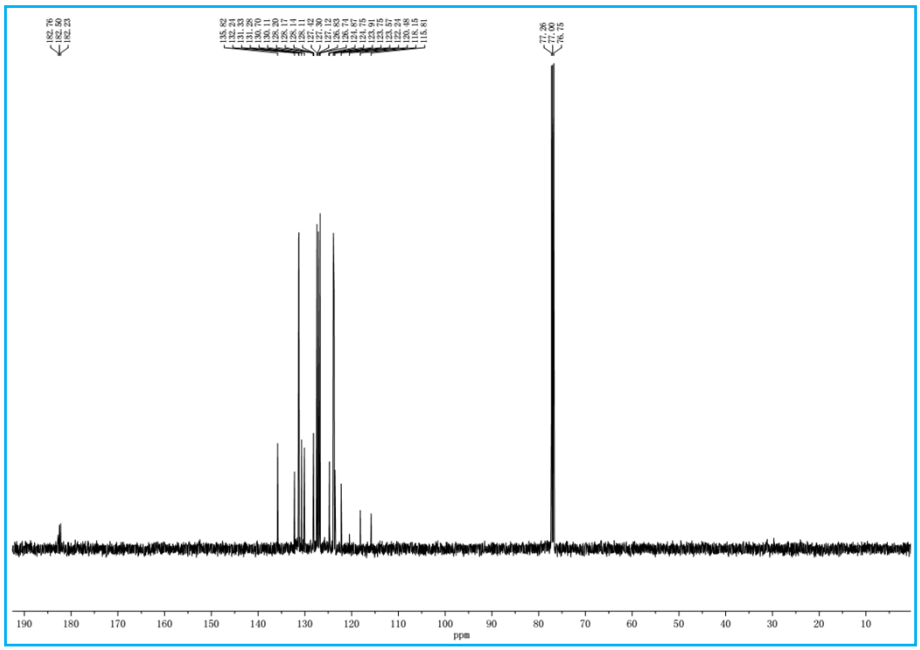

Figure S5. ^{13}C NMR spectrum of **PY-TFA** in $CDCl_3$.

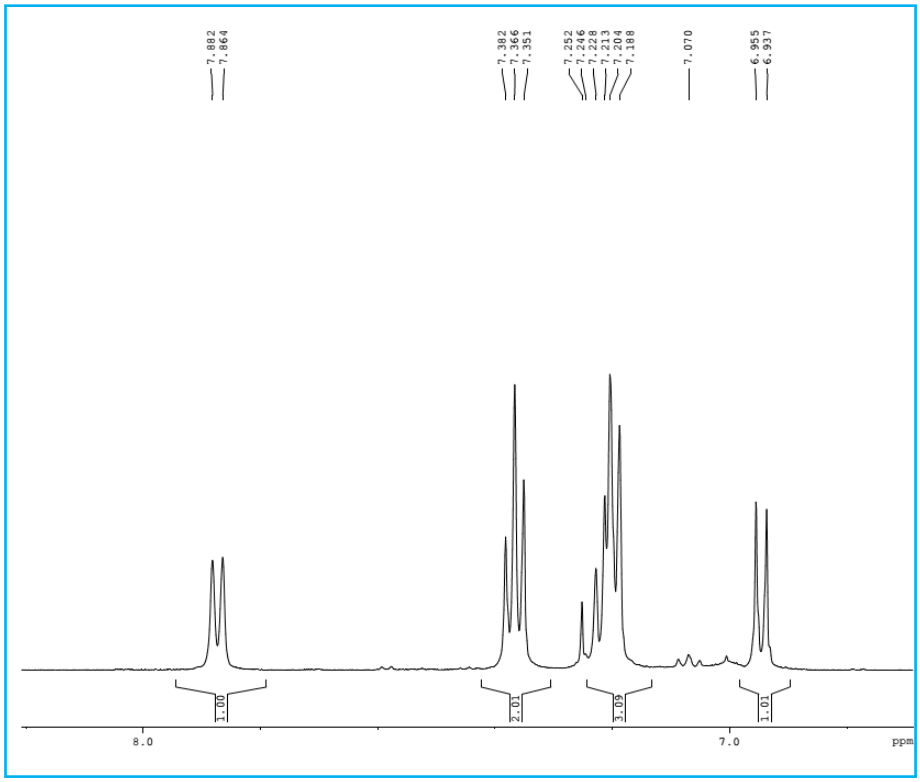

Figure S6. ^{1}H NMR spectrum of **TPA-TFA** in $CDCl_3$.

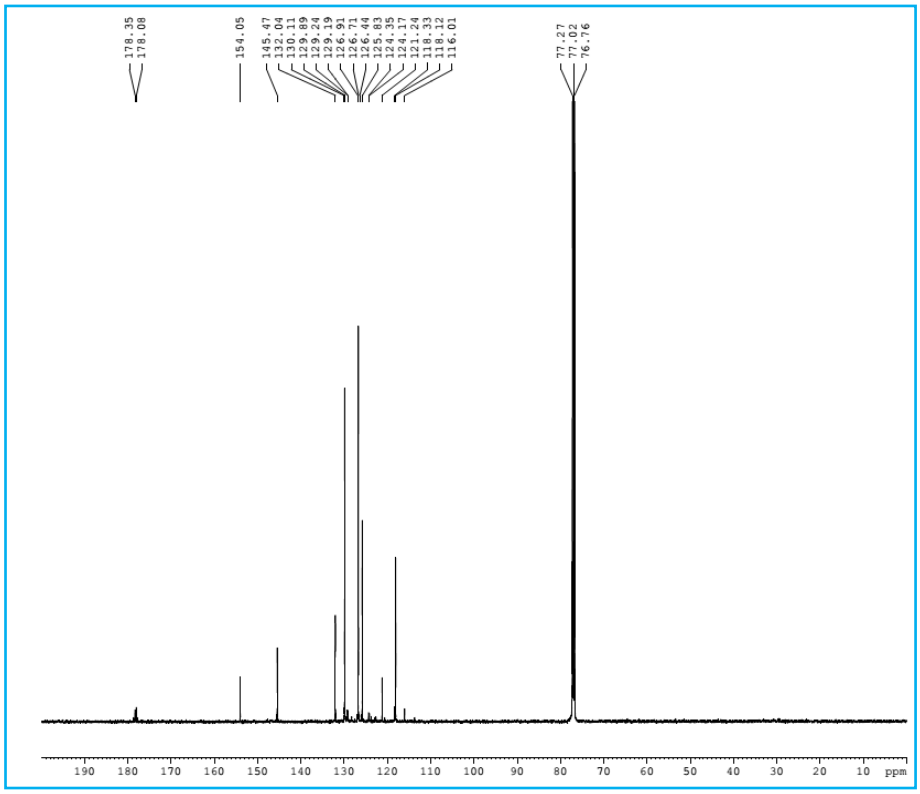

Figure S7. ^{13}C NMR spectrum of **TPA-TFA** in $CDCl_3$.

Table S1. Detail methodology and parameters of DMol3

DMol3	
Task	Geometry Optimization
Properties	Optics, Orbitals
Energy	1.0^{-5}Ha
Max. force	0.002Ha/Å
Max. displacement	0.005Å
Max. interations	50
Max. step size	0.3Å
Functional	GGA,BLYP
Integration accuracy	Fine

SCF tolerance	Fine
Core treatment	All Electron
Basis set	DNP+
Basis file	4.4
Orbital cutoff	Fine
quality	
Run in parallel on	12 cores

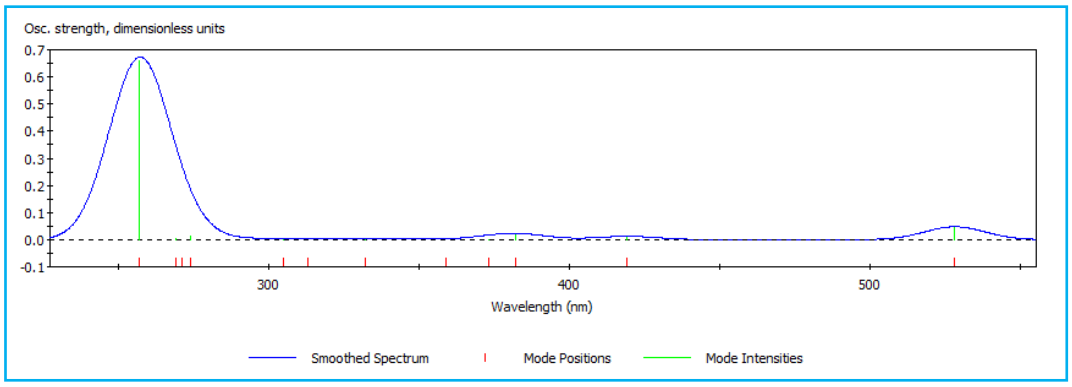

Figure S8. DMol3 optical absorption spectrum of **ANT-TFA**.

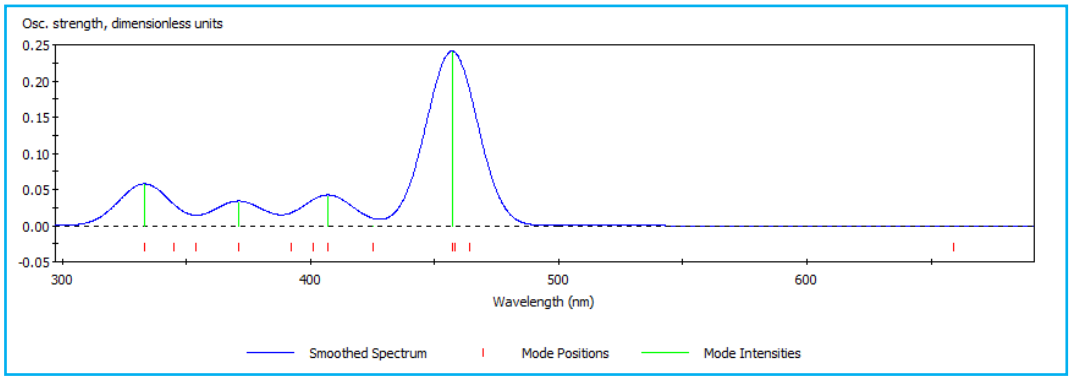

Figure S9. DMol3 optical absorption spectrum of **PY-TFA**.

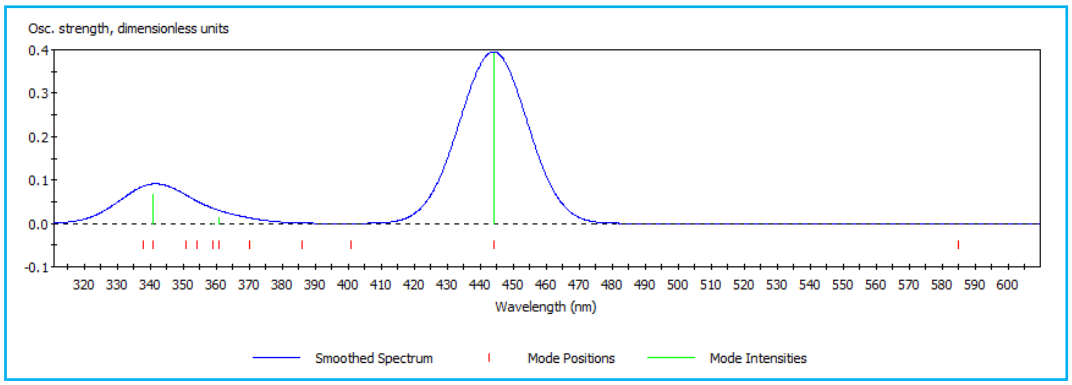

Figure S10. DMol3 optical absorption spectrum of **TPA-TFA**.

In order to confirm CT nature of the electronic transition, we choose five different solvents to carryout solvent dependent absorption and emission spectral studies of all the three dyes. The results were summarized in Table S2, S3 and Figure S11~S13.

Table S2. The absorption and fluorescence spectra of **ANT-TFA**, **PY-TFA** and **TPA-TFA** in different solvents.

Solvents	Δf	**ANT-TFA**		**PY-TFA**		**TPA-TFA**	
		$\lambda_{ab}^{max}(nm)$	$\lambda_{em}^{max}(nm)$	$\lambda_{ab}^{max}(nm)$	$\lambda_{em}^{max}(nm)$	$\lambda_{ab}^{max}(nm)$	$\lambda_{em}^{max}(nm)$
Cyclohexane	-0.00165	365	449	376	440	377	448
Toluene	0.013235	366	425	377	443	378	510
Tetrahydrofuran	0.209572	365	427	376	445	377	543
Dichloromethane	0.218391	365	427	377	456	376	558
Acetonitrile	0.305417	366	428	376	463	376	445

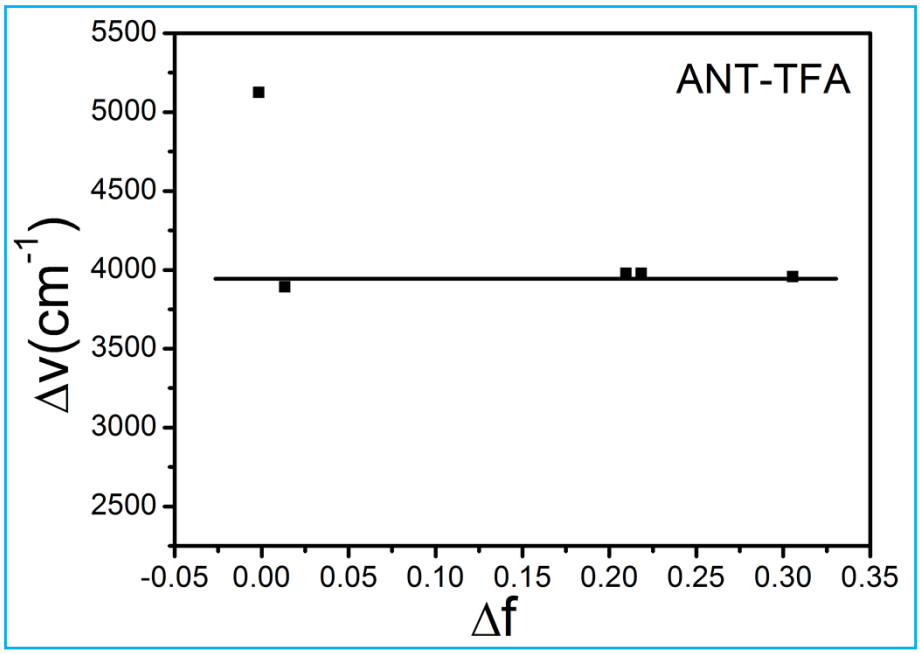

Figure S11. Lippert-Mataga equation curve of **ANT-TFA**.

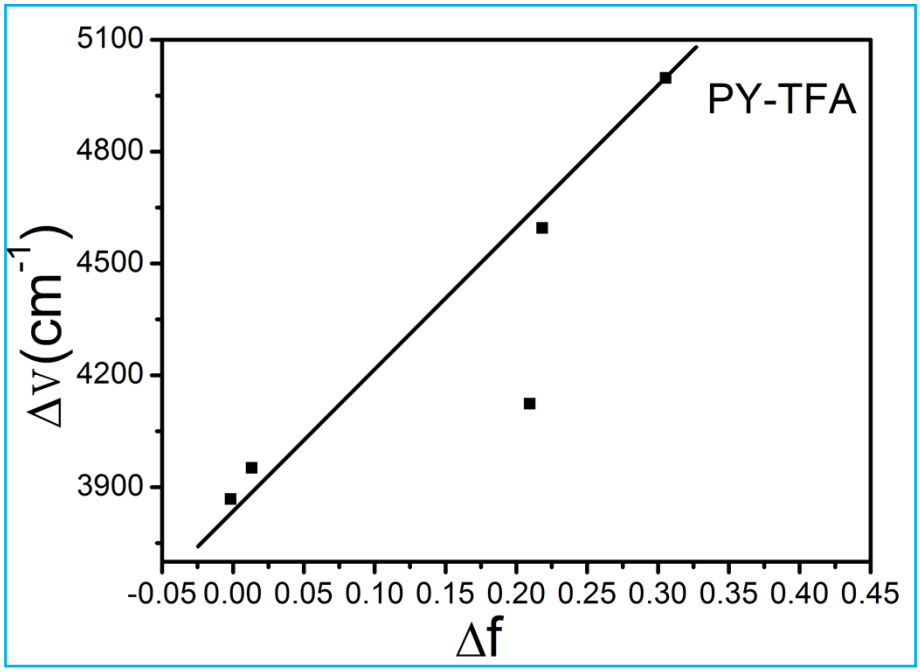

Figure S12. Lippert-Mataga equation curve of **PY-TFA**.

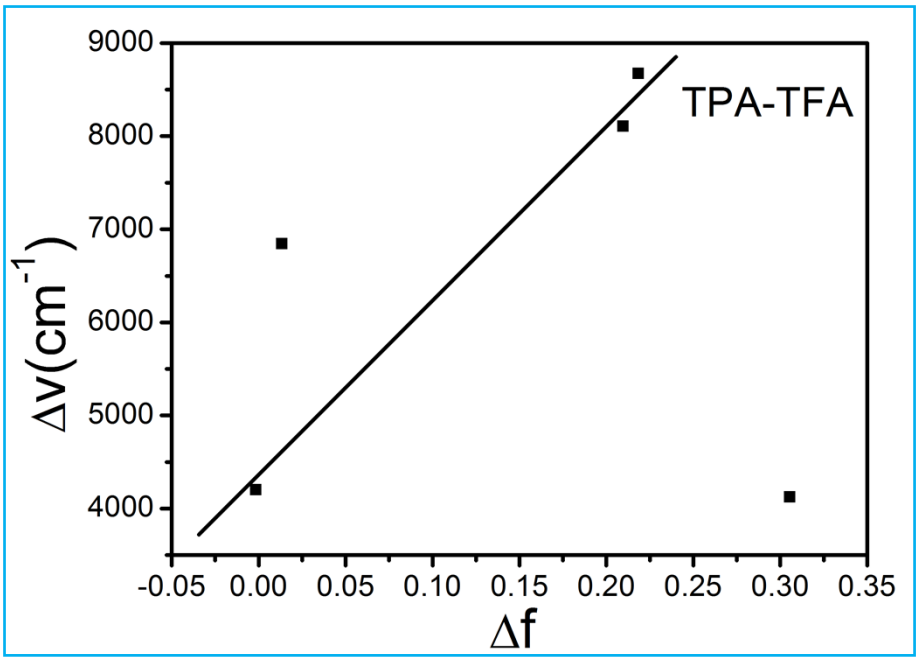

Figure S13. Lippert-Mataga equation curve of **TPA-TFA**.

Lippert-Mataga equation : $\Delta\overline{v} = \overline{v}_{abs} - \overline{v}_{f} = \frac{2\Delta f}{hca^3}(\mu_{S1} - \mu_{S0})^2 + \text{const}$

Table S3. Lippert-Mataga equation parameters of **ANT-TFA**, **PY-TFA** and **TPA-TFA**.

	h(10^{-34}J·s)	c(10^{8}m/s)	a(Å)	slope	u_{s1}-u_{s0}(10^{-25}C·m.)
ANT-TFA	6.626	3.0	4.7915	0	0
PY-TFA			5.514	3527.2	2.424
TPA-TFA			6.005	19477.8	6.475

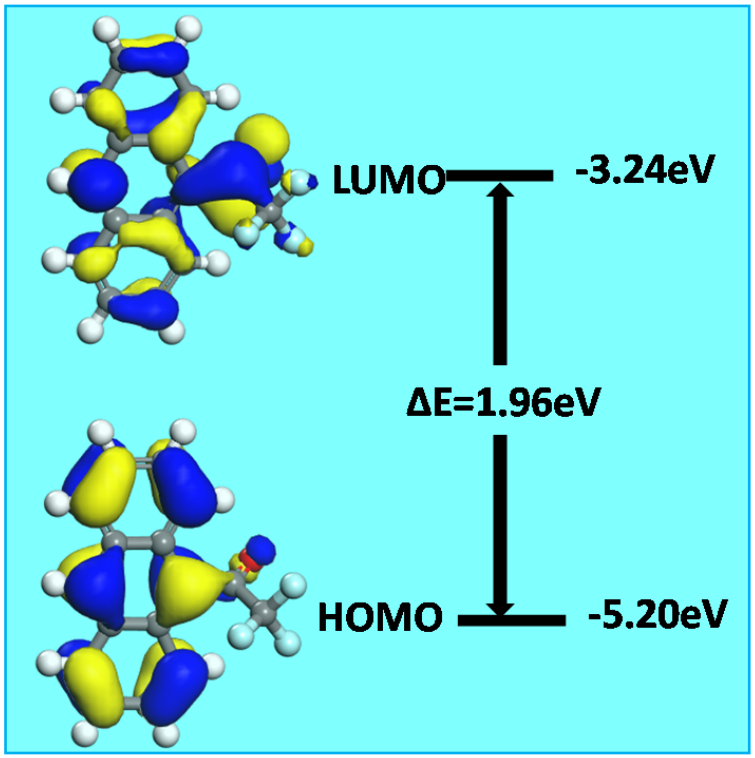

Figure S14. Optimized molecular structure and molecular orbitals of **ANT-TFA**.

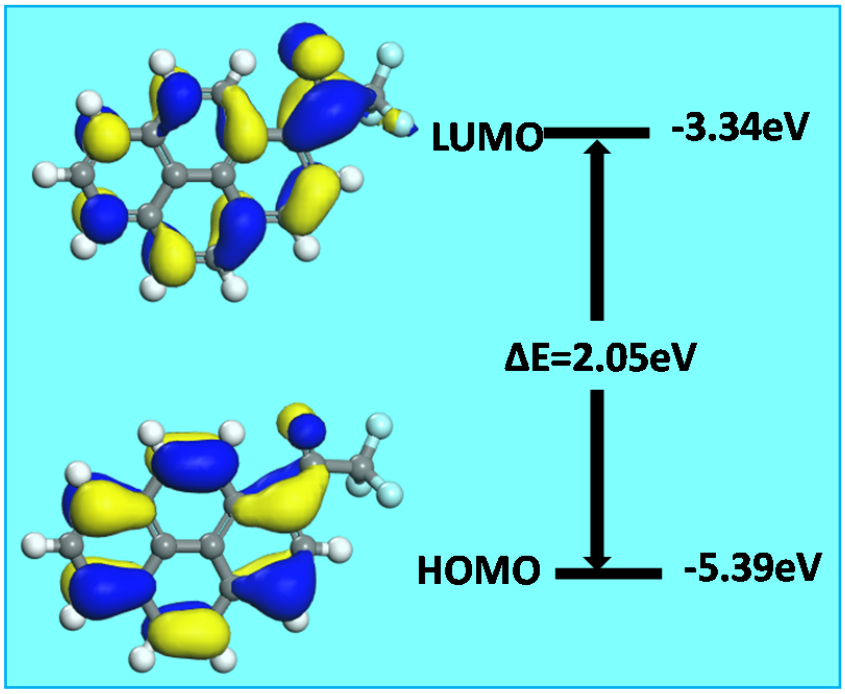

Figure S15. Optimized molecular structure and molecular orbitals of **PY-TFA**.

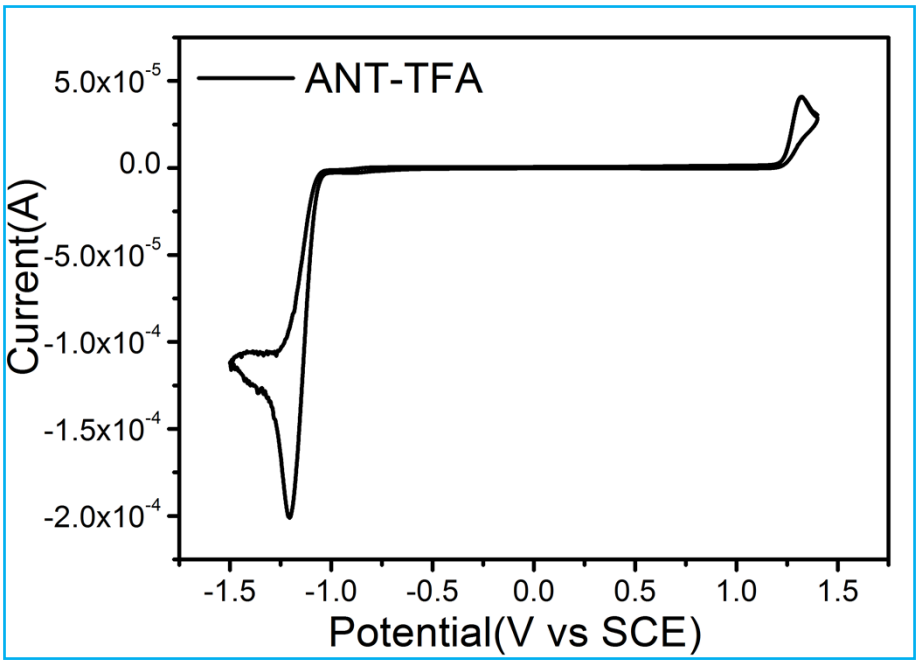

Figure S16. Cyclic voltammetric curve of **ANT-TFA**.

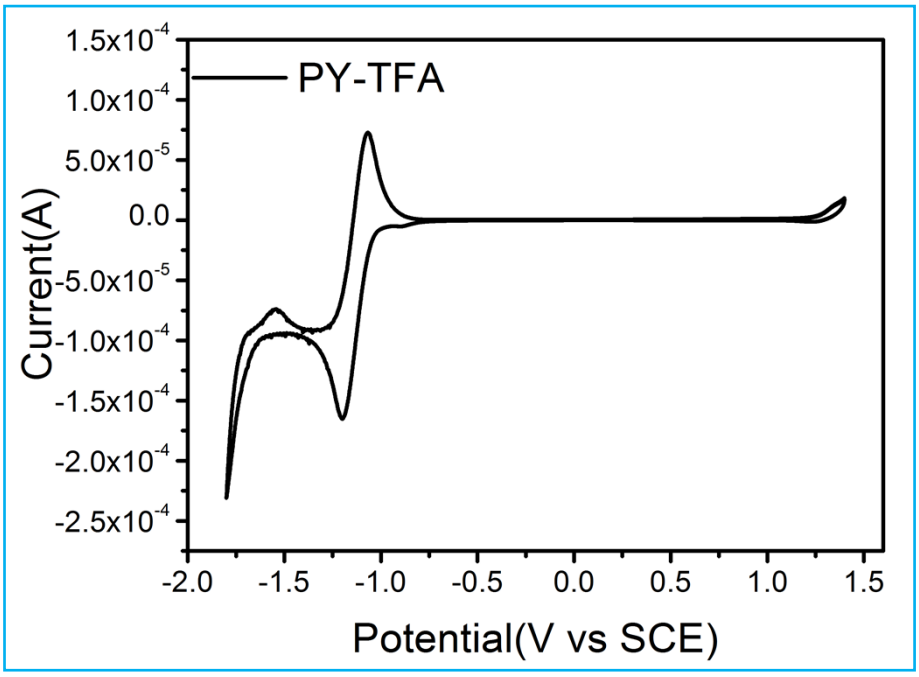

Figure S17. Cyclic voltammetric curve of **PY-TFA**.

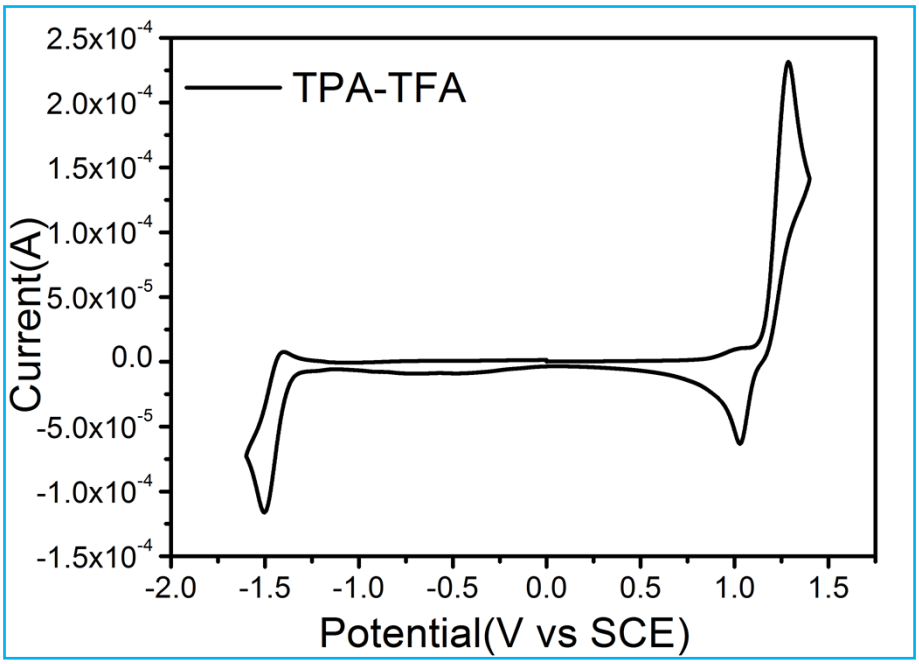

Figure S18. Cyclic voltammetric curve of **TPA-TFA**.

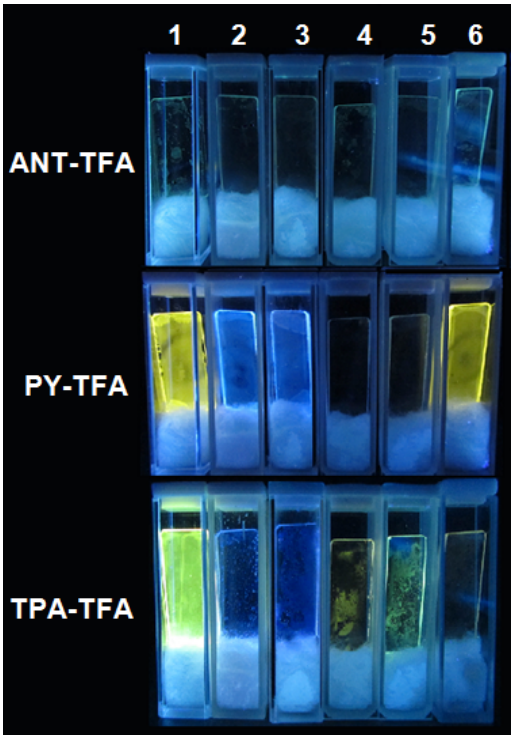

Figure S19. **ANT-TFA**, **PY-TFA**, **TPA-TFA** films excited by UV lamp 365 nm after 100s exposure in air and several saturated organic amine vapour (1 air, 2 *iso*butylamine, 3 *n*-octylamine, 4 di*iso*propylamine, 5 dipentylamine, 6 *o*-toluidine).

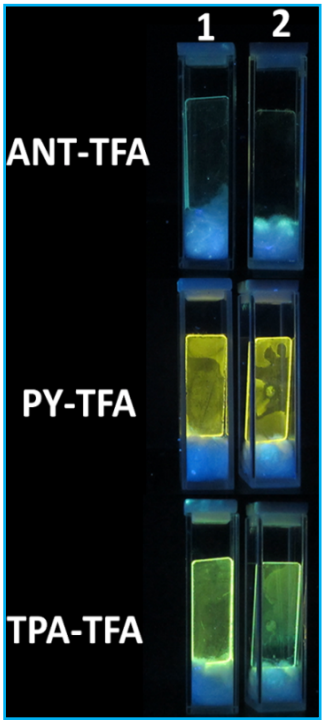

Figure S20. **ANT-TFA**, **PY-TFA**, **TPA-TFA** films excited by UV lamp 365nm after 100s exposure in air and aliphatic tertiary amine vapour (1 air, 2 triethylamine).

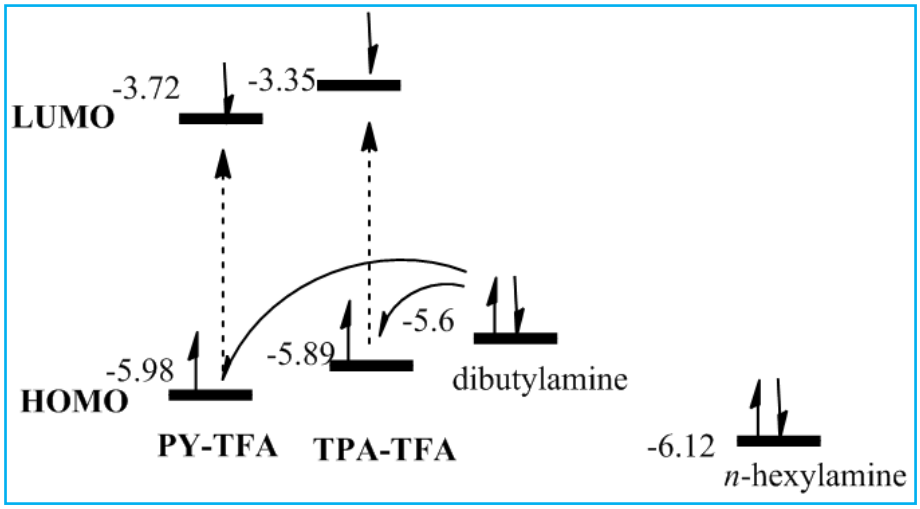

Figure S21. Photoinduced electron transfer mechanism for secondary amine sensing.

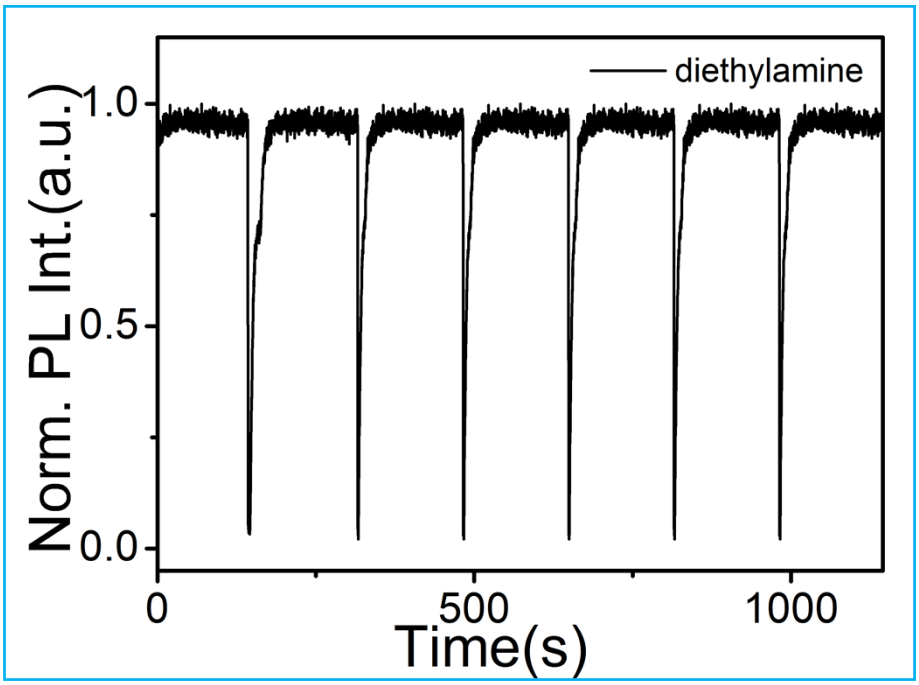

Figure S22. Repeatability of **TPA-TFA** film exposed to diethylamine vapour, the emission intensity was monitored at 525 nm.

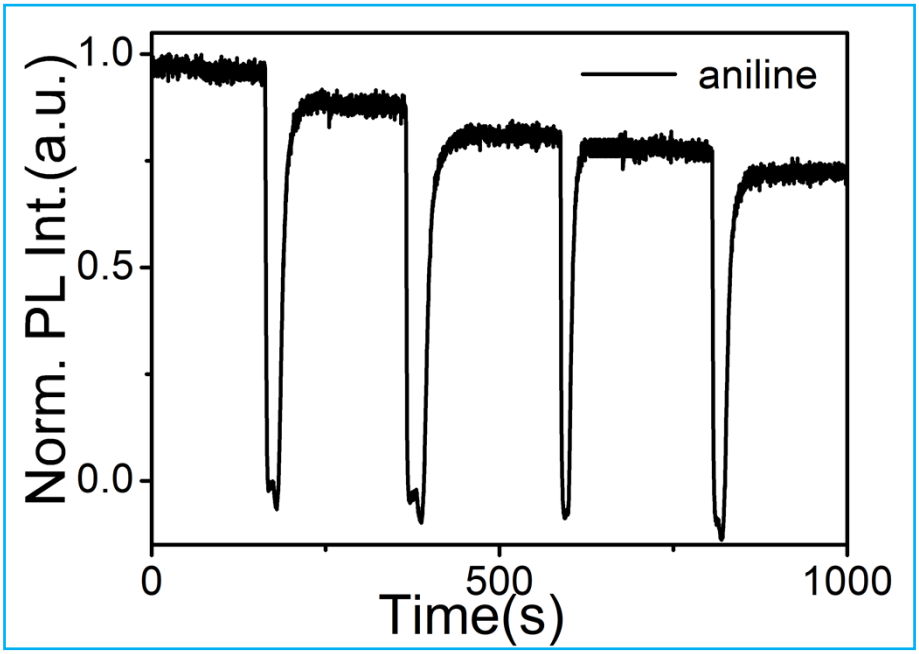

Figure S23. Repeatability of **TPA-TFA** film exposed to aniline vapour, the emission intensity was monitored at 525 nm.

Figure S24~S28 showed the time-course fluorescence responses of **TPA-TFA** films exposed to the different concentrations of amine vapour: All the first exposures were at the saturated vapour pressure of different amines at 20°C (Table S4), after elution with air, the next exposure was at a half-diluted concentration of the previous vapour. All the emission intensities were monitored at 525 nm.

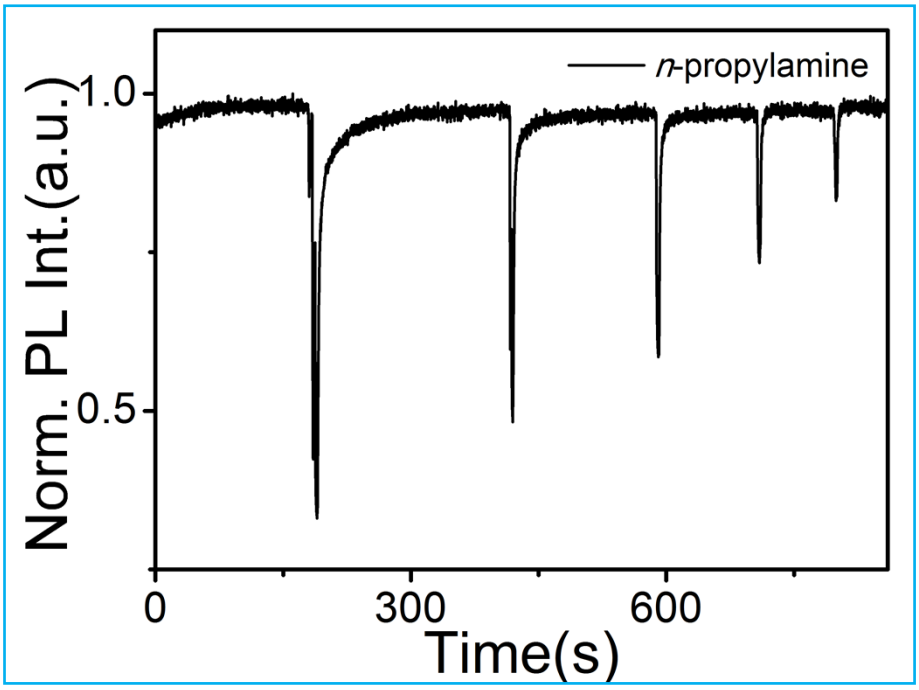

Figure S24. Time-course fluorescence responses of **TPA-TFA** films exposed to the different concentrations of *n*-propylamine vapour.

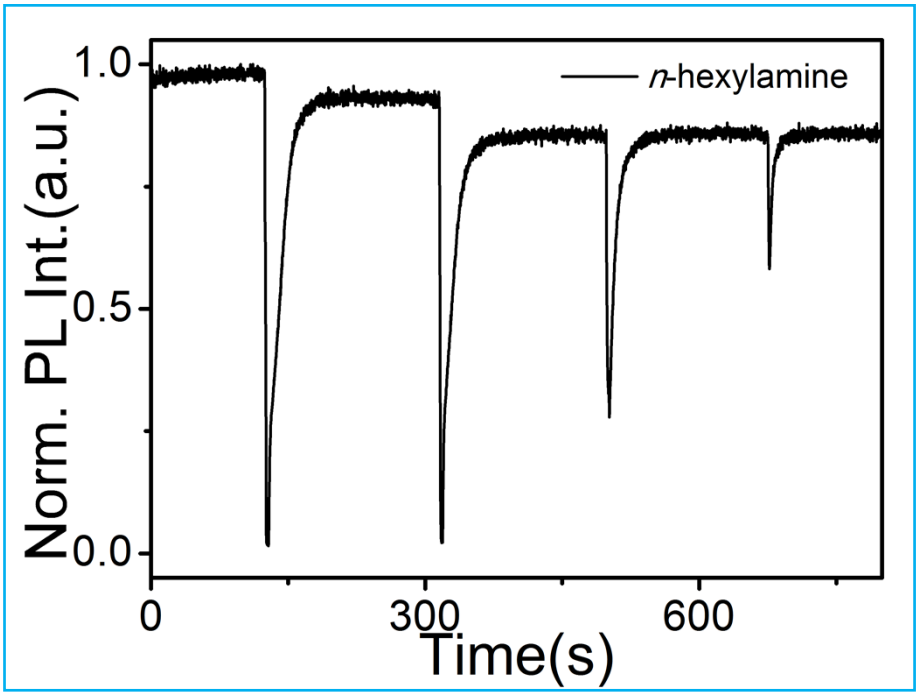

Figure S25. Time-course fluorescence responses of **TPA-TFA** films exposed to the different concentrations of *n*-hexylamine vapour.

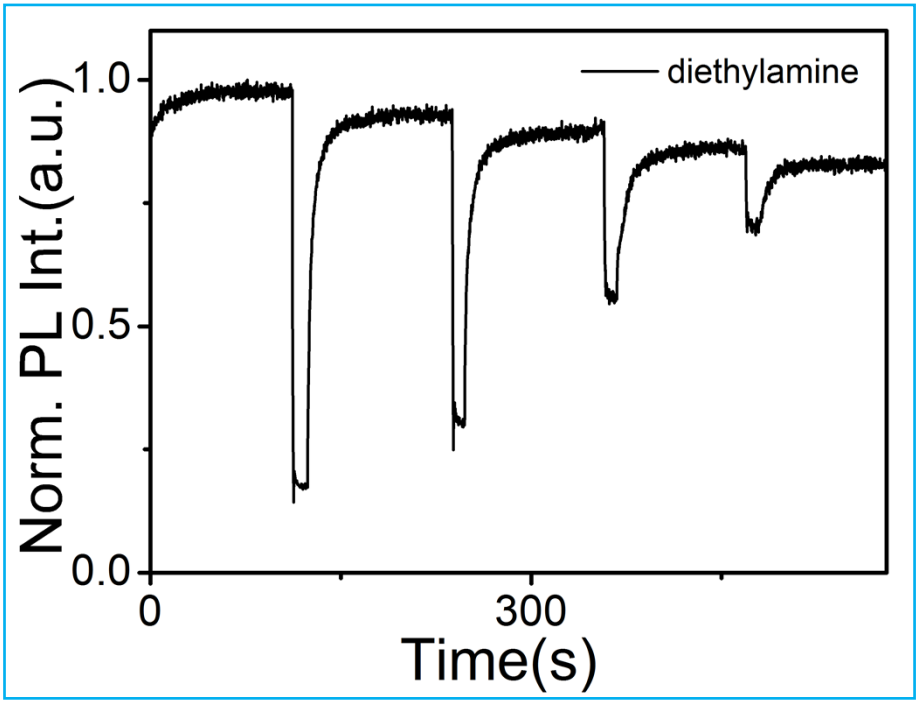

Figure S26. Time-course fluorescence responses of **TPA-TFA** films exposed to the different concentrations of diethylamine vapour.

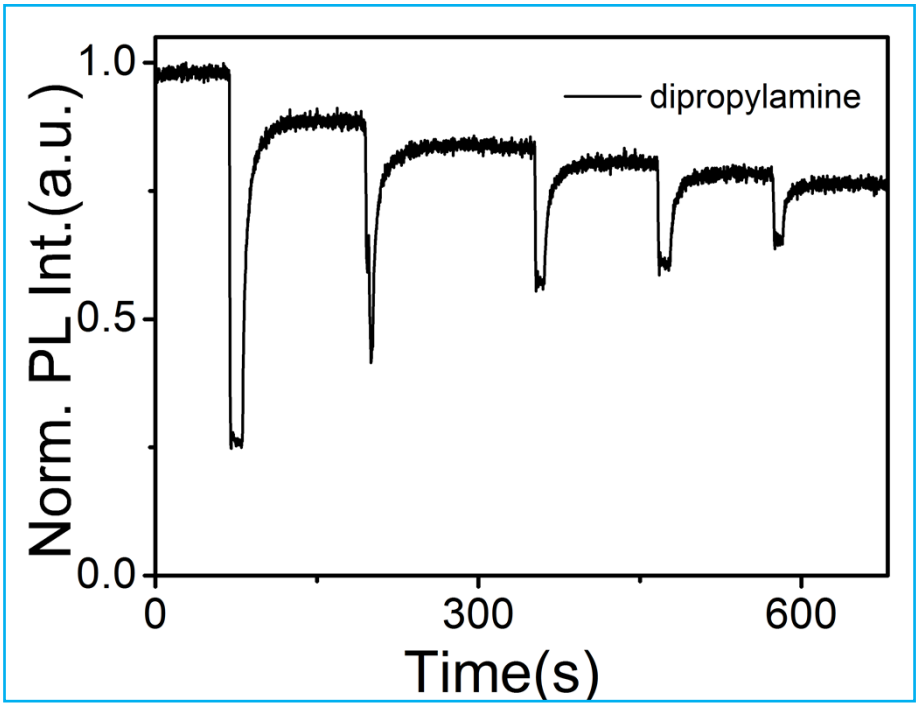

Figure S27. Time-course fluorescence responses of **TPA-TFA** films exposed to the different concentrations of dipropylamine vapour.

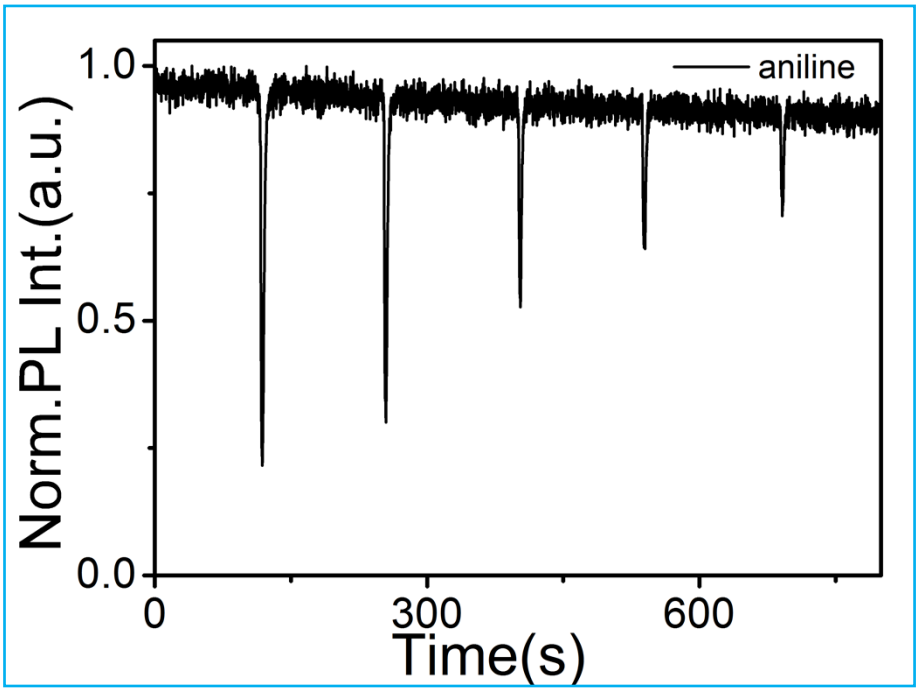

Figure S28. Time-course fluorescence responses of **TPA-TFA** films exposed to the different concentrations of aniline vapour.

Table S4. The saturated vapour pressure of different amines at 20°C.

amine	saturated vapour pressure(ppm)
n-propylamine	3.25×10^{5}
n-hexylamine	8.78×10^{3}
diethylamine	2.48×10^{5}
dipropylamine	2.36×10^{4}
aniline	557.12

Table S5. Detection limit of **PY-TFA** and **TPA-TFA** films exposed to different amines.

amine	detection limit (ppm)	
	TPA-TFA	**PY-TFA**
n-propylamine	0.01	3.51
n-hexylamine	5.01	0.98
diethylamine	1.73×10^{-4}	2.04
dipropylamine	0.198	1.55
aniline	2.35×10^{-4}	/

We obtained the IDLH concentrations from the official data published by the Centers for Disease Control and Prevention, USA. The web link is as bellow: http://www.cdc.gov/niosh/idlh/.