Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
This journal is © The Royal Society of Chemistry 2021

Supplementary Information

Dual-Emission Ratiometric Fluorescent Probe based Lanthanide-Functionalized Hydrogen-Bonded Organic Framework for Visual Detection of Methylamine

Yanhong Liu,[a] Xin Xu[a], Haifeng Lu,*,[b] and Bing Yan*,[a]

[a] School of Chemical Science and Engineering, Tongji University, Shanghai 200092, China

[b] School of Chemistry and Chemical Engineering, Shandong University, South Shanda Road 27, Jinan 250100, P. R. China.

E-mail: lhf@sdu.edu.cn; byan@tongji.edu.cn.

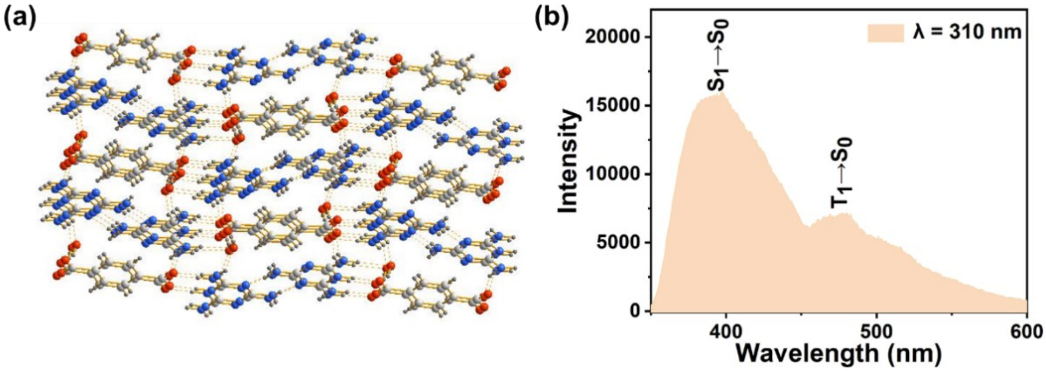


Figure S1. (a) Framework of D-A dual-component Tt-TPA. (b) Emission spectra of Tt-TPA (λ_{ex} = 310 nm).

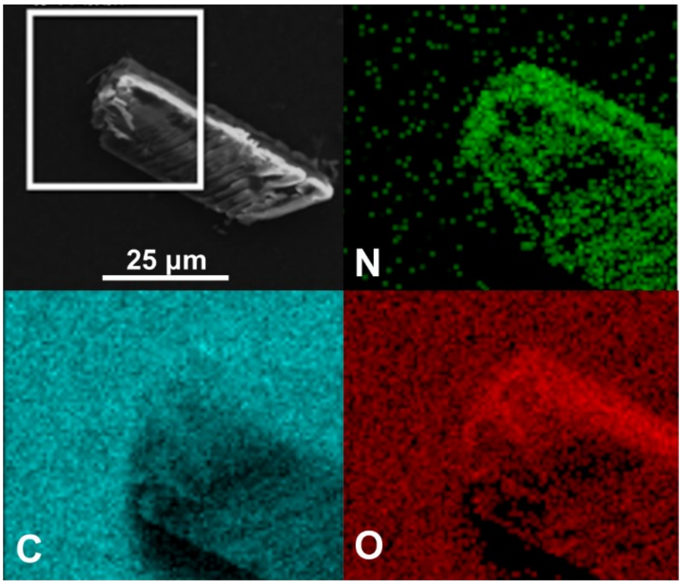


Figure S2. SEM pictures of Tt-TPA and the corresponding elemental distribution mapping. Scale bars: 25 μm.

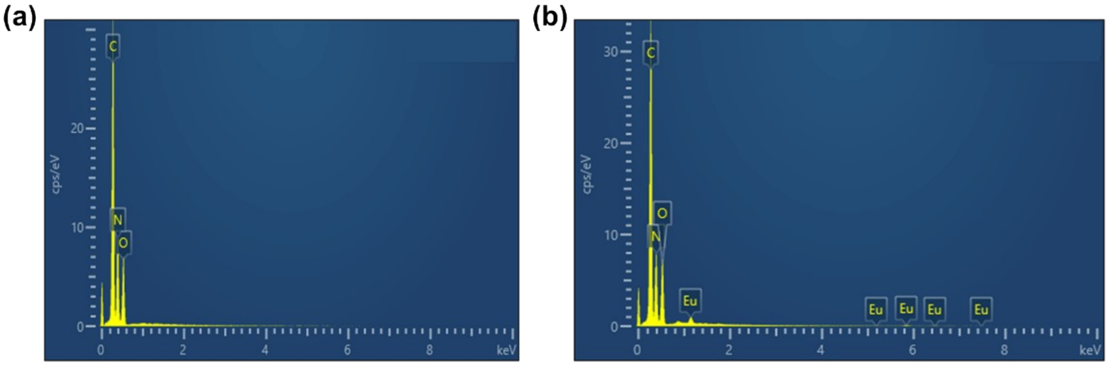


Figure S3. EDX spectra of Tt-TPA (a) and Eu@Tt-TPA (b).

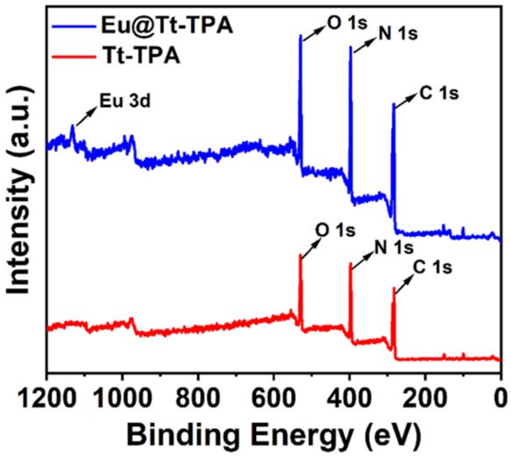


Figure S4. XPS spectra of Tt-TPA (red line) and Eu@Tt-TPA (blue line).

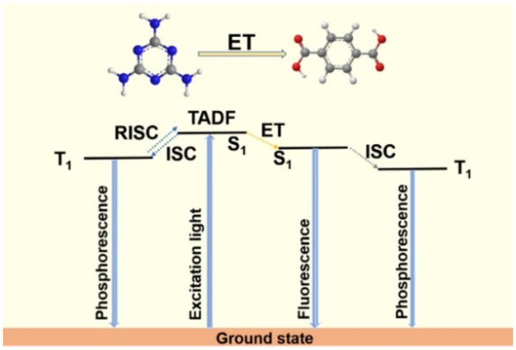


Figure S5. Schematic diagram for RTP mechanism: TAD Fassisted energy transfer from Tt to TPA moiety. (ISC: intersystem crossing; RISC: reverse intersystem crossing; TADF: thermally activated delayed fluorescence)

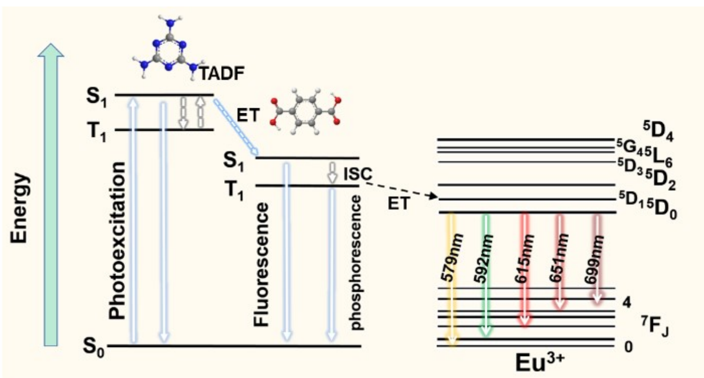


Figure S6. Schematic diagram for TADF-assisted ET and LMCT-induced ET progresses for Eu@Tt-TPA (ISC: intersystem crossing; TADF: thermally activated delayed fluorescence).

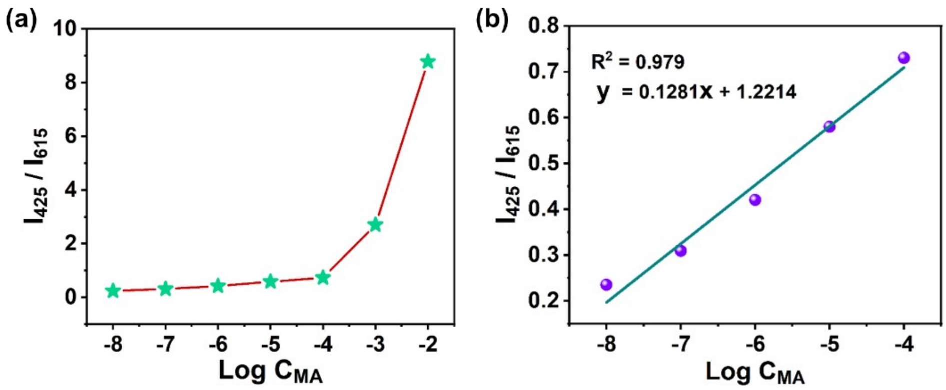


Figure S7. (a) Plot of the intensity ratio of I_{425}/I_{615} (Eu@Tt-TPA) vs MA concentration. (b) Calibration curves of Eu@Tt-TPA added MA in aqueous solution with different concentrations (10^{-8}–10^{-4} M).

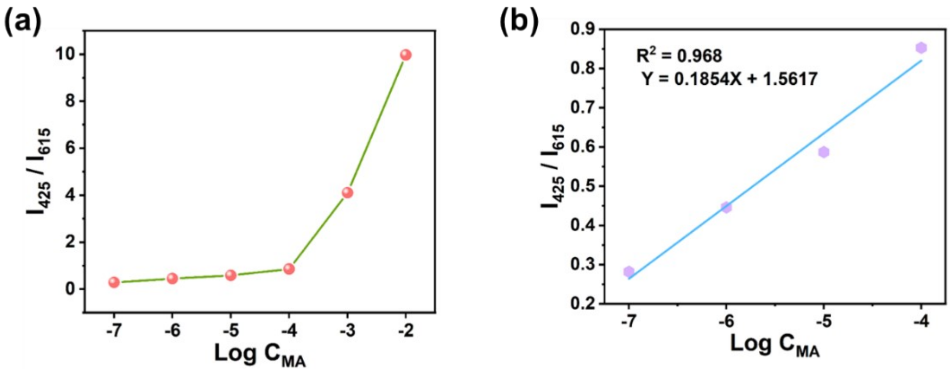


Figure S8. (a) Plot of the intensity ratio of I_{425}/I_{615} (Eu@Tt-TPA film) vs MA concentration. (b) Linear relationship between the concentration of MA (10^{-7}–10^{-4} M) and the variation of the ratio under the single excitation of 310 nm.

Figure S9. Photos of Eu@Tt-TPA with MA or a series of aliphatic amines, aniline and ammonia under 310 nm UV-light irradiation. The concentrations of MA and a series of aliphatic amines, aniline and ammonia were 10^{-2} M.

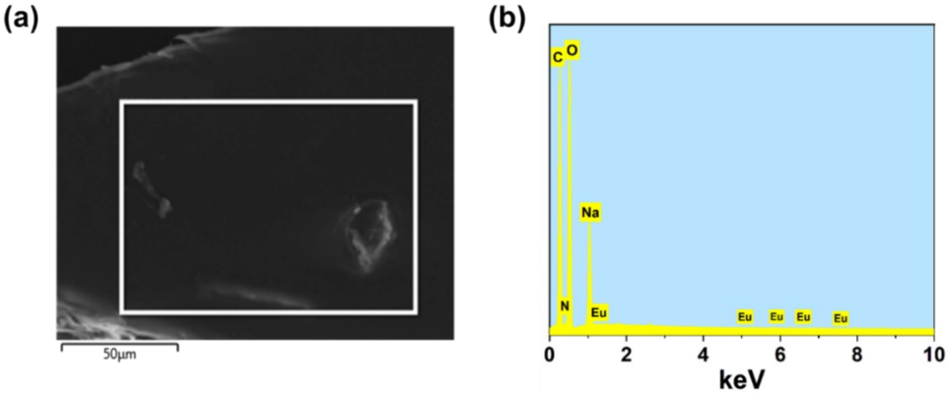


Figure S10. (a) SEM image of Eu@Tt-TPA film. (b) The element content of C (42.35%), N (4.24%), O (45.09%), Eu (0.87%) and Na (7.45%) elements in EDX energy spectrum of Eu@Tt-TPA film.

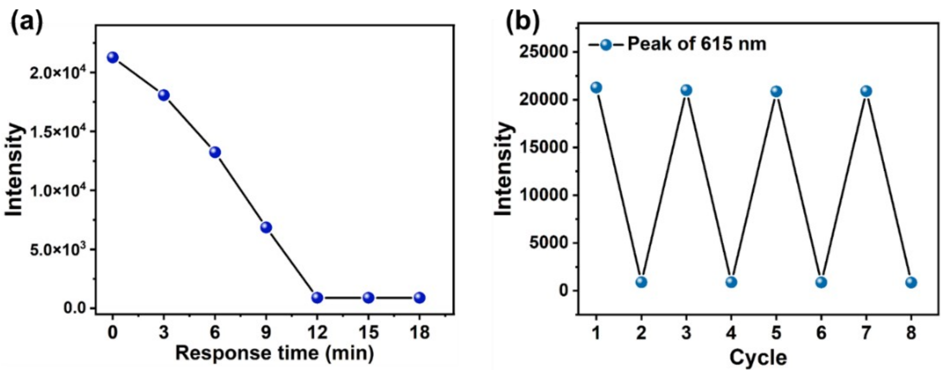


Figure S11. (a) Time-dependent luminescence intensity of Eu@Tt-TPA film at 615 nm. (b) The luminescence intensity of Eu@Tt-TPA film after four recycles.

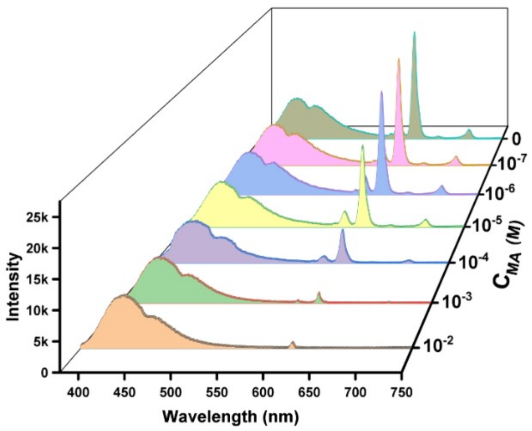


Figure S12. Emission spectra (λ_{ex} = 310 nm) of Eu@Tt-TPA film exposure to various concentrations MA.

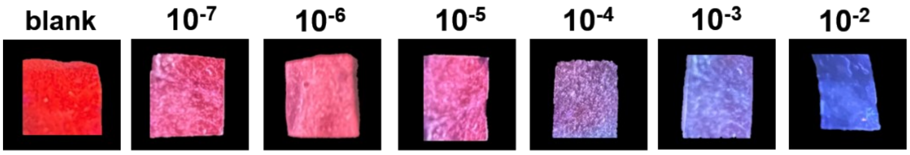


Figure S13. Photos of Eu@Tt-TPA film after exposure to various concentrations MA (10^{-7}–10^{-2} M) under 310 nm UV-light irradiation.

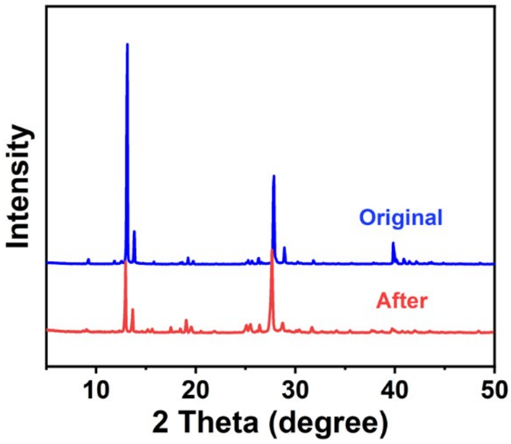


Figure S14. PXRD patterns of Eu@Tt-TPA before and after sensing MA.

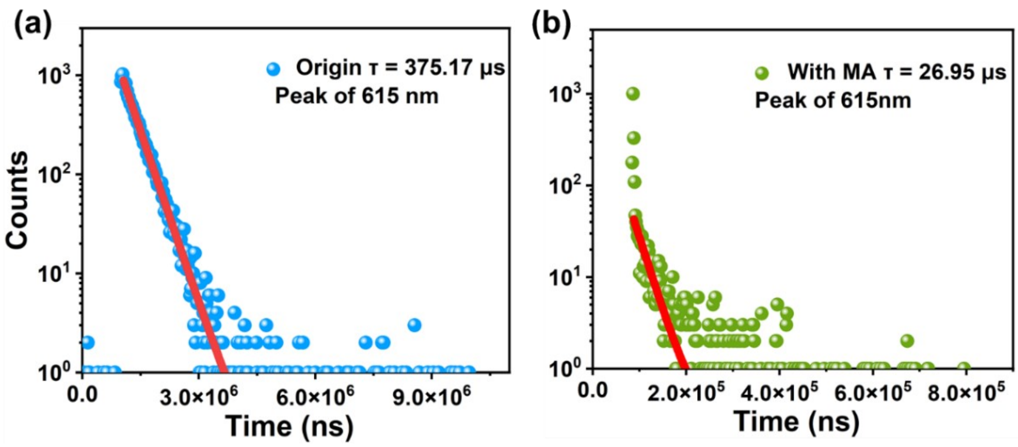


Figure S15. Luminescence decay curves of Eu@Tt-TPA (a) and Eu@Tt-TPA + MA (b) (λ_{ex} = 310 nm, λ_{em} = 615 nm).

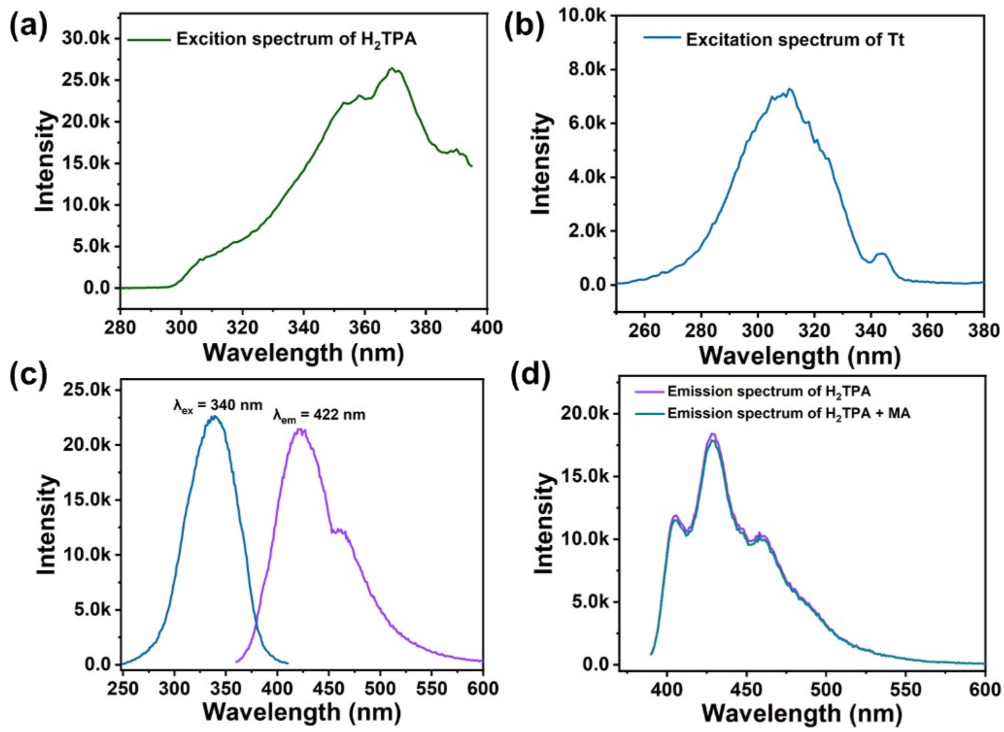


Figure S16. (a) Excitation spectra of H_2TPA (λ_{em} = 430 nm). (b) Excitation spectrum of Tt (λ_{em} = 369 nm). (c) Excitation and emission spectra of MA. (d) Emission spectrum of H_2TPA and H_2TPA +MA (λ_{ex} = 369 nm) .

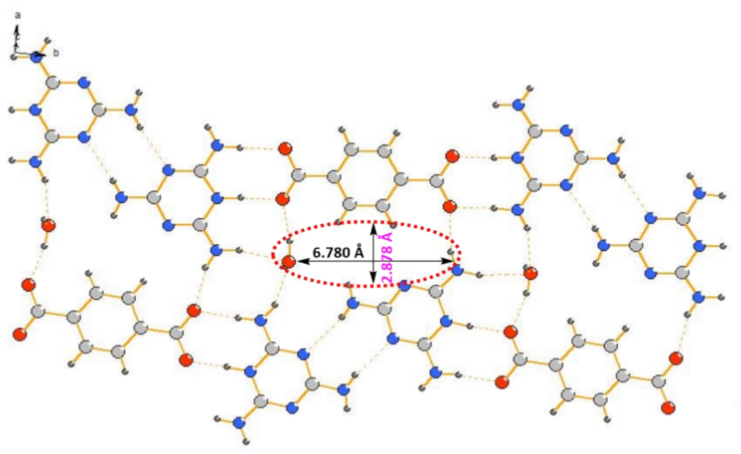


Figure S17. (a) Excitation spectra of H_2TPA (λ_{em} = 430 nm). (b) Excitation spectrum of Tt (λ_{em} = 369 nm).

Table S1. The weight percentage of all elements in Tt-TPA and Eu@Tt-TPA determined by EDX.

Element	Percentage by weight	
	Tt-TPA	Eu@Tt-TPA
C	38.77	40.76
N	39.78	33.92
O	21.45	19.29
Eu	……	6.04

Table S2. Summary of excitation transitions and experimental energy gaps of Tt, MA, H_2TPA and Eu^{3+}.

	Transitions	Wavelength (nm)	Energy gap (eV)
Tt	$S_0 \rightarrow S_n$	311	3.99
MA	$S_0 \rightarrow S_n$	340	3.65
H_2TPA	$S_0 \rightarrow S_n$	368	3.37
	$^5D_0 \rightarrow {}^7F_0$	579	2.14
	$^5D_0 \rightarrow {}^7F_1$	592	2.09
Eu^{3+}	$^5D_0 \rightarrow {}^7F_2$	615	2.02
	$^5D_0 \rightarrow {}^7F_3$	652	1.91
	$^5D_0 \rightarrow {}^7F_4$	696	1.78

Table S3. Summary of excitation transitions and experimental energy gaps of substrate.

Substrate	Transitions	Wavelength (nm)	Energy gap (eV)
ammonia	$S_0 \rightarrow S_n$	308	4.03
ethylamine	$S_0 \rightarrow S_n$	311	3.99
aniline	$S_0 \rightarrow S_n$	324	3.83
diethylamine	$S_0 \rightarrow S_n$	348	3.56
triethylamine	$S_0 \rightarrow S_n$	351	3.53
n-hexylamine	$S_0 \rightarrow S_n$	360	3.44
ethylenediamine	$S_0 \rightarrow S_n$	372	3.33
propylamine	$S_0 \rightarrow S_n$	375	3.31

Table S4. Molecular size of amine and ammonia.

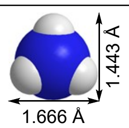
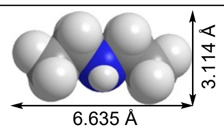
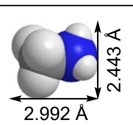
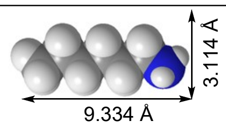
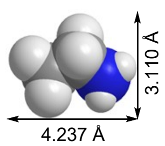
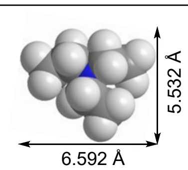
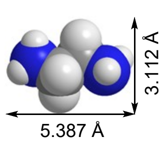
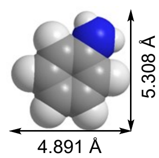
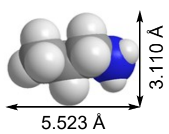
<table>
<tr><th>Entry</th><th>Substrate</th><th>Molecular size</th><th>Entry</th><th>Substrate</th><th>Molecular size</th></tr>
<tr><td>1</td><td>ammonia</td><td></td><td>6</td><td>diethylamine</td><td></td></tr>
<tr><td>2</td><td>methylamine</td><td></td><td>7</td><td>n-hexylamine</td><td></td></tr>
<tr><td>3</td><td>ethylamine</td><td></td><td>8</td><td>triethylamine</td><td></td></tr>
<tr><td>4</td><td>ethylenediamine</td><td></td><td>9</td><td>aniline</td><td></td></tr>
<tr><td>5</td><td>propylamine</td><td></td><td></td><td></td><td></td></tr>
</table>

Table S5. Determination of MA in water samples.

Sample	MA added (μmol/L)	MA found (μmol/L)	Recovery (%)	R.S.D. (n = 3) (%)
Tap water	0.1	0.104	104	2.25
	5	4.869	97.38	3.48
	10	10.281	102.81	1.89
River water	0.1	0.096	96	2.18
	5	5.121	102.42	1.92
	10	10.513	105.13	4.02