Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Design, synthesis and properties of a reactive chromophoric/ fluorometric probe for hydrogen peroxide detection

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Catalogue

Supporting Information..1

1 Table S1. Detail methodology and parameters of DMol3..............3

2 ^{1}H-NMR spectra, ^{13}C-HMR spectra and Mass spectra...................4

4 Boronate oxidation reaction..9

3 Figures for detailed sensing performance.......................................9

4 Detail information about linear fit..10

5 DMol3 optical absorption spectrum of Anthracene, AVP, and AVPM...11

6 The selectivity of fluorescent probe 12

7 Detection limit measurements 12

8 A summary of chromophoric/flourescent probes for hydrogen peroxide detection...13

Reference 14

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 quality	Fine
Run in parallel on	12 cores

2 ^{1}H-NMR spectra, ^{13}C-HMR spectra and Mass spectra

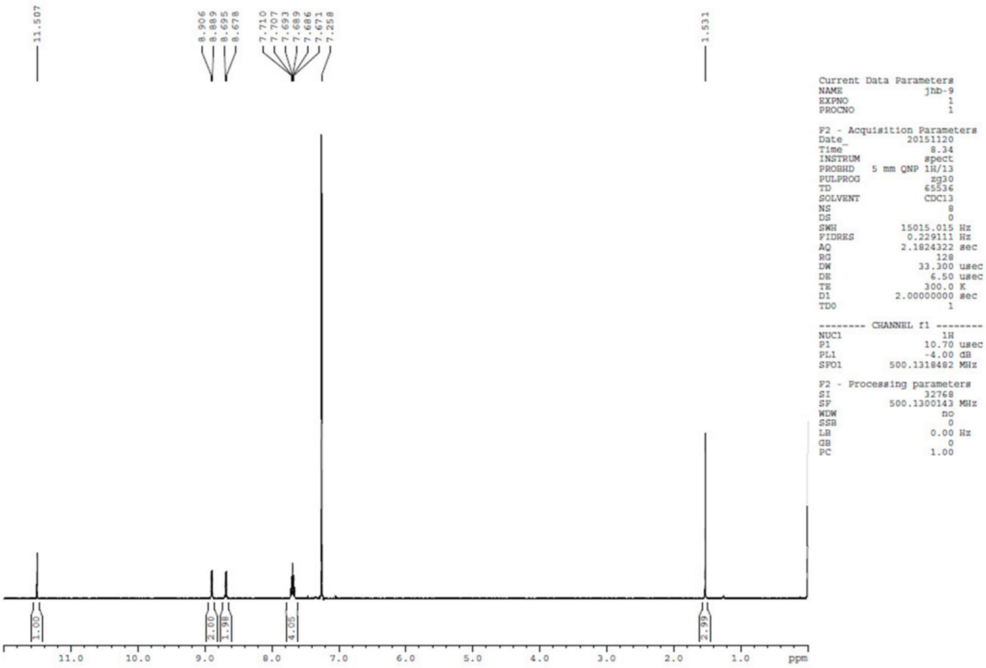


Figure S1. ^{1}H-NMR spectra of 10-bromoanthracene-9-carbaldehyde **1**.

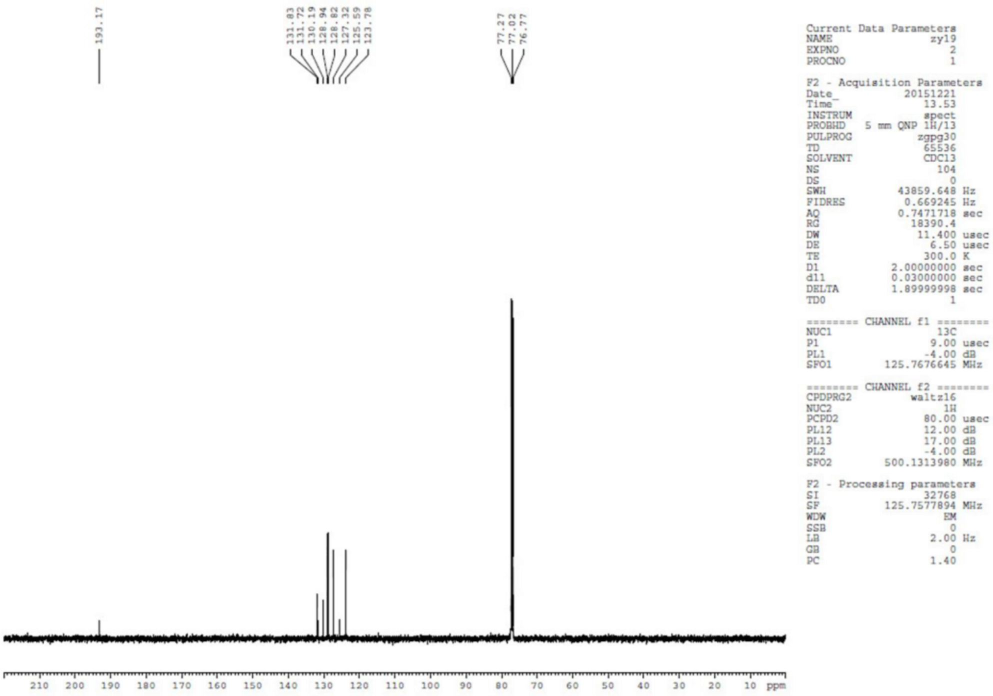
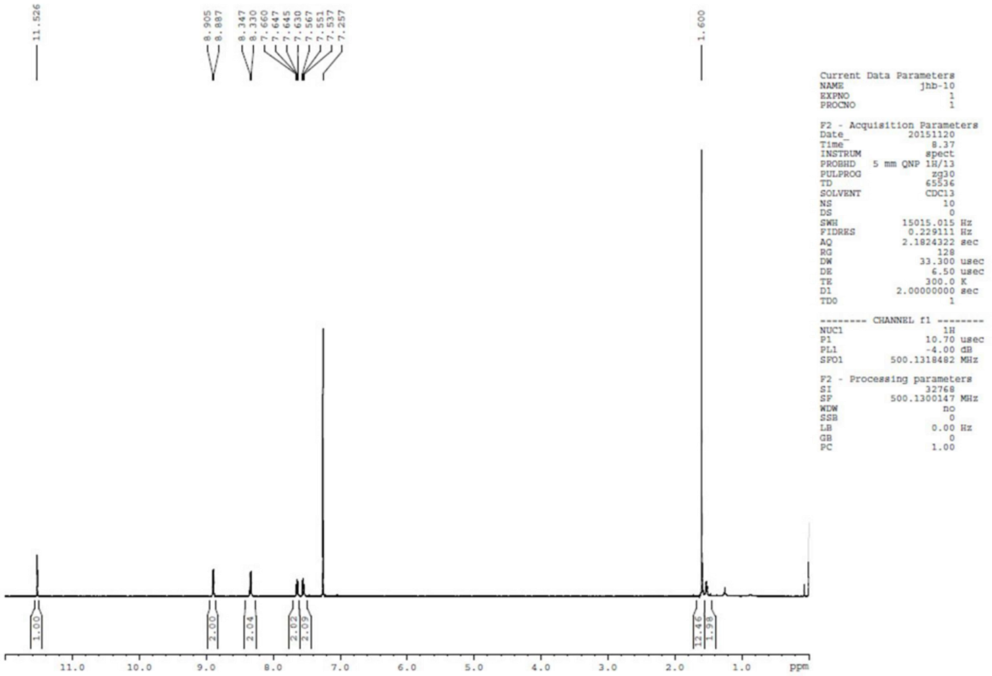


Figure S2. ^{13}C-HMR spectra of 10-bromoanthracene-9-carbaldehyde **1**.



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PROCNO                 1

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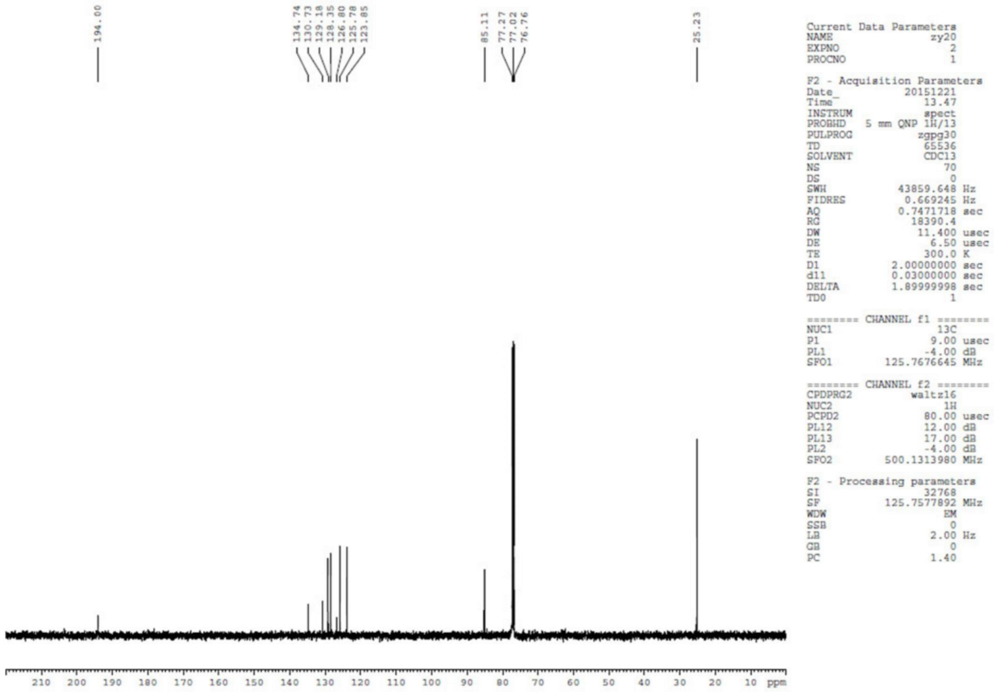
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    10
DS                     0
SWH            15015.015 Hz
FIDRES          0.229111 Hz
AQ             2.1824322 sec
RG                   128
DW                33.300 usec
DE                  6.50 usec
TE                 300.0 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.70 usec
PL1                -4.00 dB
SFO1         500.1318482 MHz

F2 - Processing parameters
SI                 32768
SF           500.1300147 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```

Figure S3. ^{1}H-NMR spectra of 10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)anthracene-9-carbaldehyde **2**.



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TD                 65536
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FIDRES          0.669245 Hz
AQ             0.7471718 sec
RG               18390.4
DW                11.400 usec
DE                  6.50 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

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PL1                -4.00 dB
SFO1         125.7676645 MHz

======== CHANNEL f2 ========
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NUC2                  1H
PCPD2              80.00 usec
PL12               12.00 dB
PL13               17.00 dB
PL2                -4.00 dB
SFO2         500.1313980 MHz

F2 - Processing parameters
SI                 32768
SF           125.7577892 MHz
WDW                   EM
SSB                    0
LB                  2.00 Hz
GB                     0
PC                  1.40
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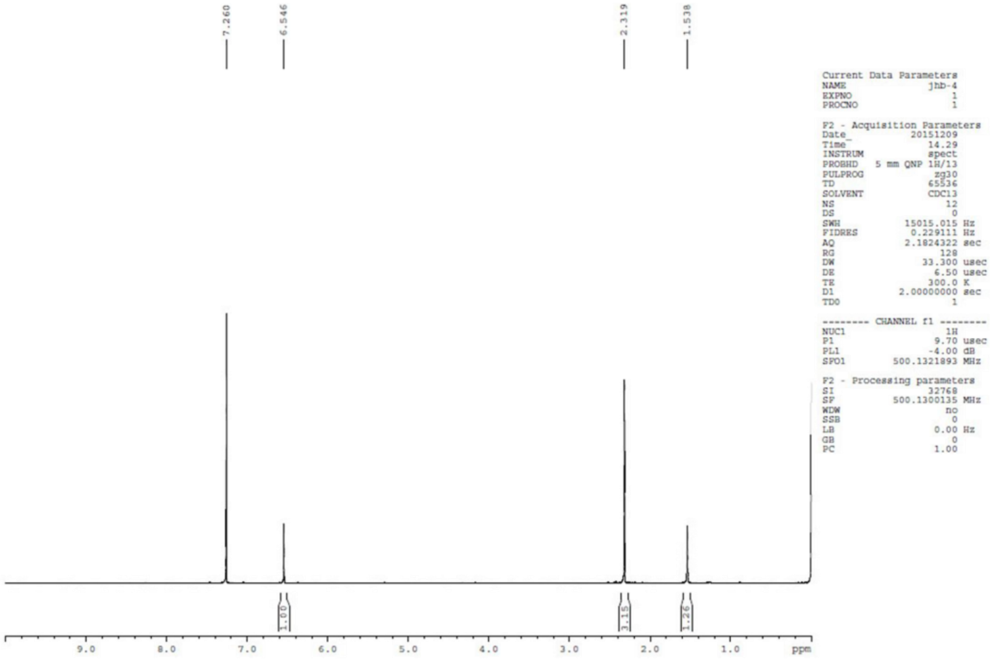
Figure S4. ^{13}C-HMR spectra of 10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)anthracene-9-carbaldehyde **2**.



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PROCNO                 1

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PULPROG             zg30
TD                 65536
SOLVENT            CDC13
NS                    12
DS                     0
SWH            15015.015 Hz
FIDRES          0.229111 Hz
AQ             2.1824322 sec
RG                   128
DW                33.300 usec
DE                  6.50 usec
TE                 300.0 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
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PL1                -4.00 dB
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F2 - Processing parameters
SI                 32768
SF           500.1300135 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
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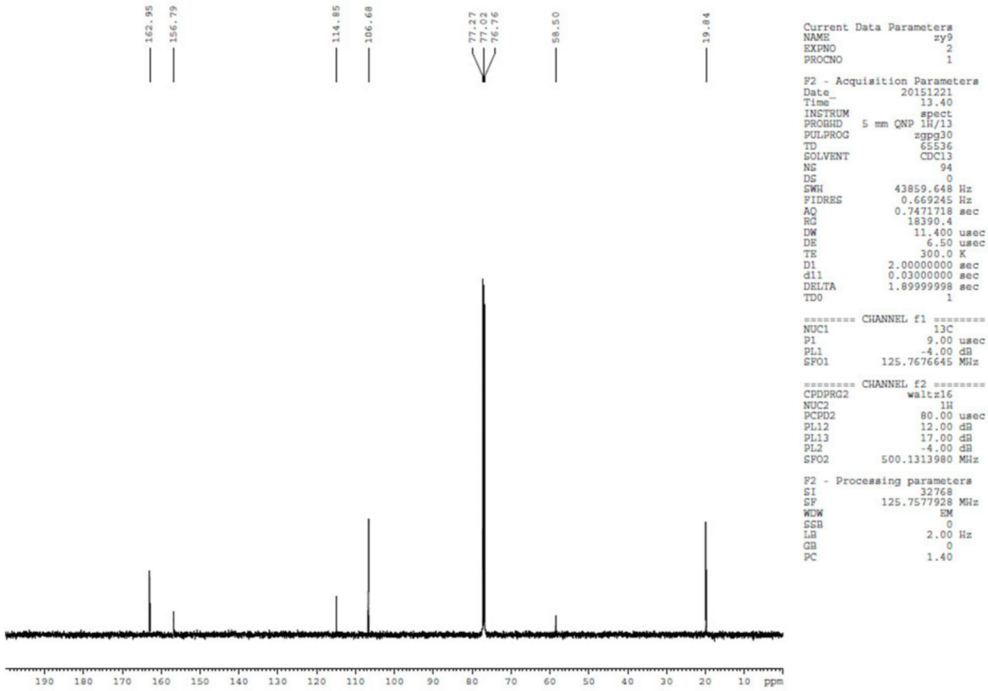
Figure S5. ^{1}H-NMR spectra of 2-(2,6-dimethyl-4H-pyran-4-ylidene)malononitrile **3**.



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EXPNO                  2
PROCNO                 1

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PULPROG           zgpg30
TD                 65536
SOLVENT            CDC13
NS                    94
DS                     0
SWH            43859.648 Hz
FIDRES          0.669245 Hz
AQ             0.7471718 sec
RG               18390.4
DW                11.400 usec
DE                  6.50 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.00 usec
PL1                -4.00 dB
SFO1         125.7676645 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL12               12.00 dB
PL13               17.00 dB
PL2                -4.00 dB
SFO2         500.1313980 MHz

F2 - Processing parameters
SI                 32768
SF           125.7577928 MHz
WDW                   EM
SSB                    0
LB                  2.00 Hz
GB                     0
PC                  1.40
```

Figure S6. ^{13}C-HMR spectra of 2-(2,6-dimethyl-4H-pyran-4-ylidene)malononitrile **3**.

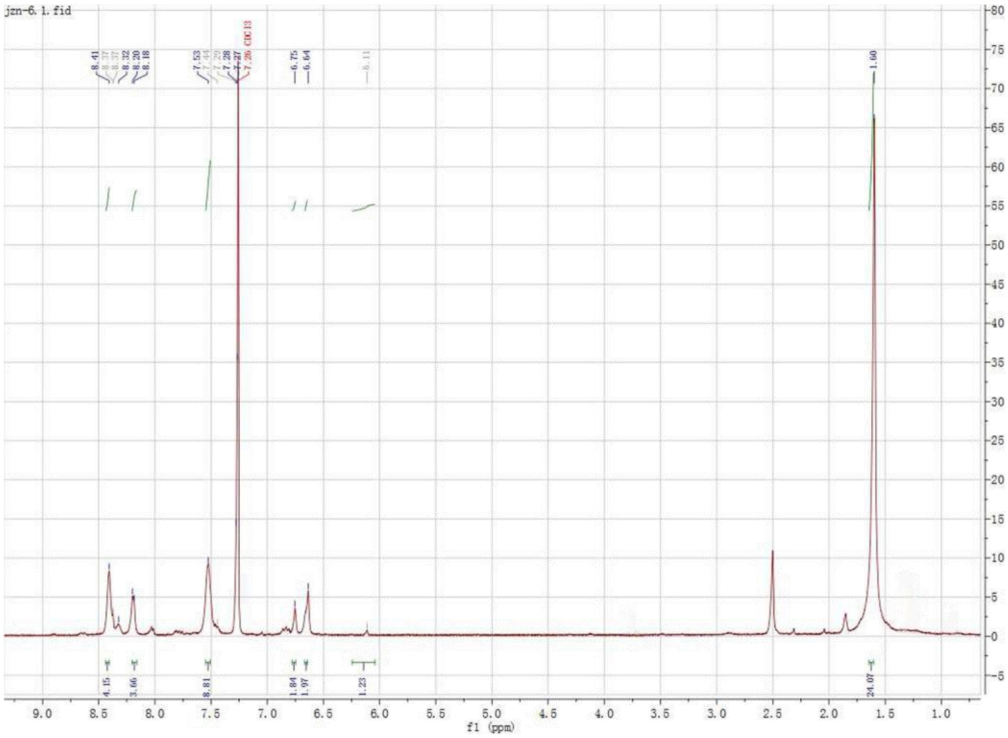
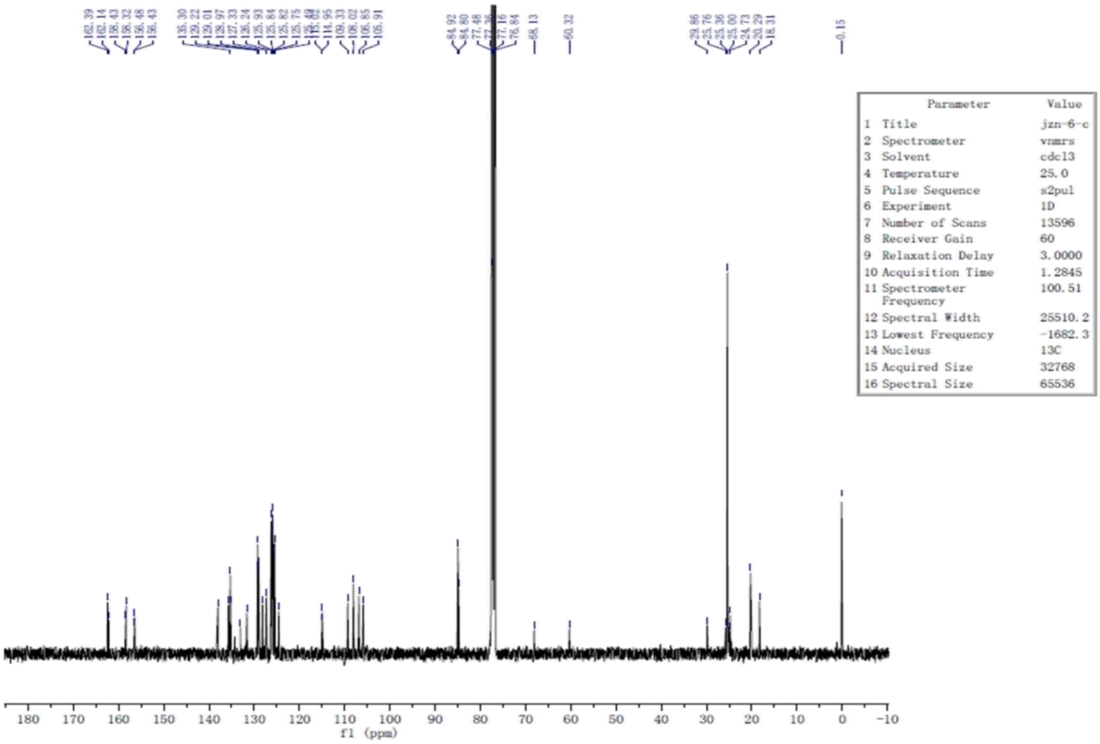


Figure S7. ^{1}H-NMR spectra of 2-(2,6-bis((E)-2-(10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) anthracen-9-yl)vinyl)-4H-pyran-4-ylidene)malononitrile **AVPM**.



	Parameter	Value
1	Title	jzn-6-c
2	Spectrometer	vnmrs
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Number of Scans	13596
8	Receiver Gain	60
9	Relaxation Delay	3.0000
10	Acquisition Time	1.2845
11	Spectrometer Frequency	100.51
12	Spectral Width	25510.2
13	Lowest Frequency	−1682.3
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536

Figure S8. ^{13}C-HMR spectra of 2-(2,6-bis((E)-2-(10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) anthracen-9-yl)vinyl)-4H-pyran-4-ylidene)malononitrile **AVPM**.

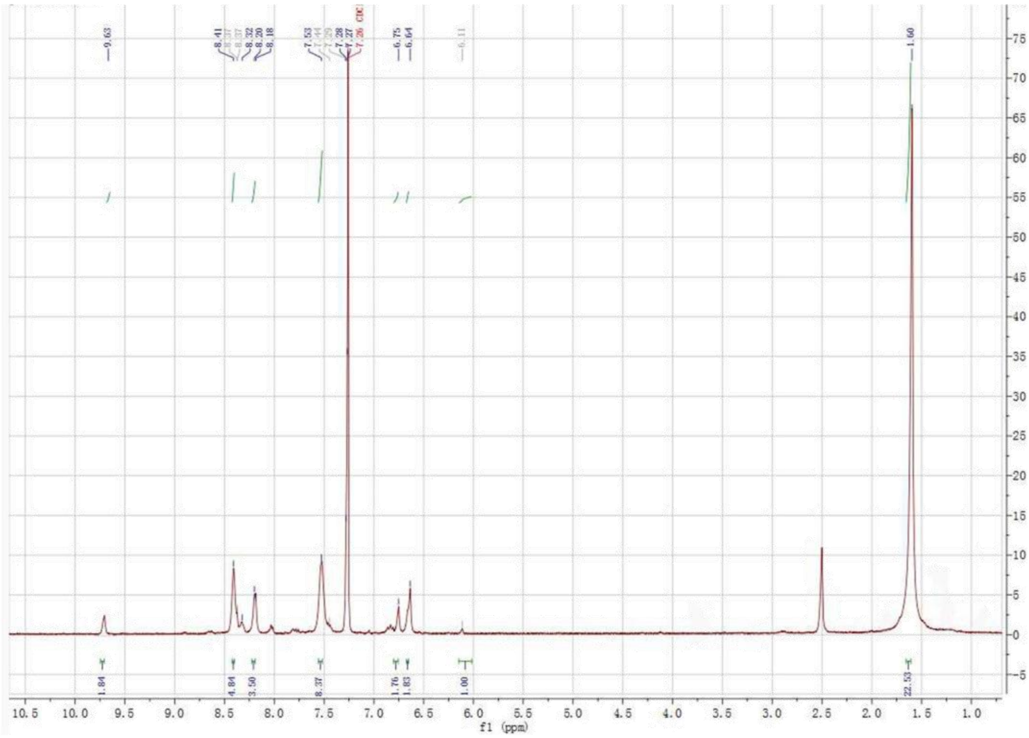


Figure S9. ^{1}H-NMR spectra of 2-(2,6-bis((E)-2-(10-hydroxyanthracen-9-yl)vinyl)-4H-pyran-4-ylidene)malononitrile **HAVPM**.

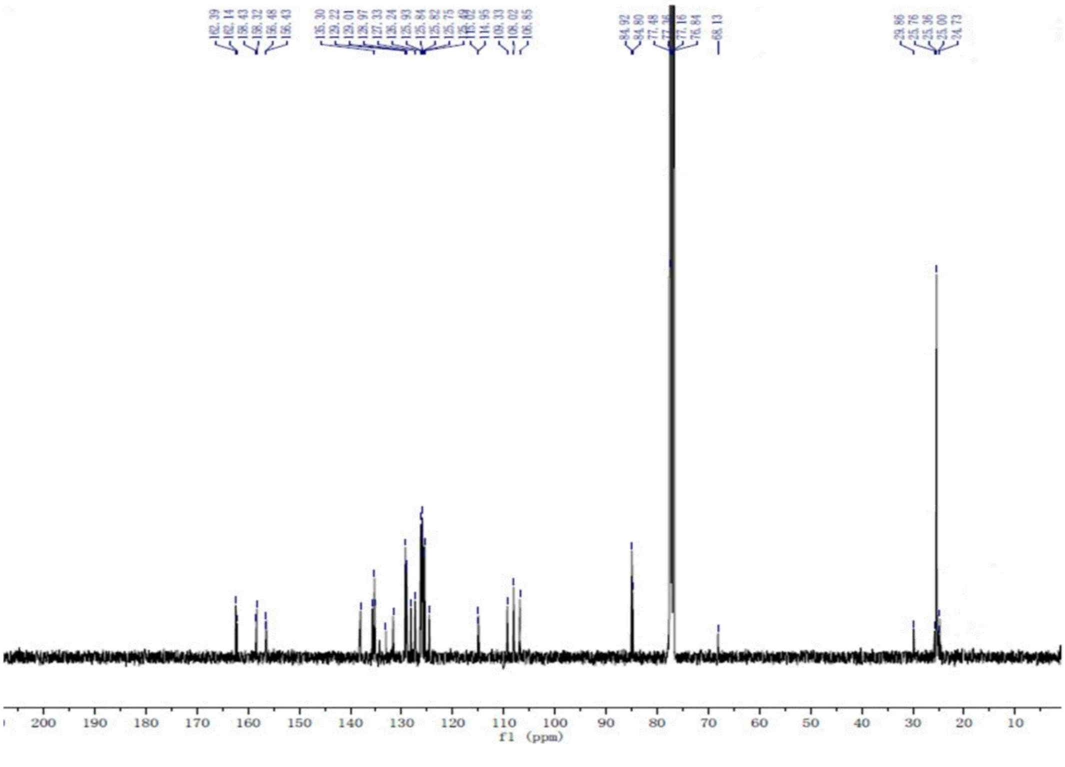


Figure S10. ^{13}C-NMR spectra of 2-(2,6-bis((E)-2-(10-hydroxyanthracen-9-yl)vinyl)-4H-pyran-4-ylidene)malononitrile **HAVPM**.

4 Boronate oxidation reaction.

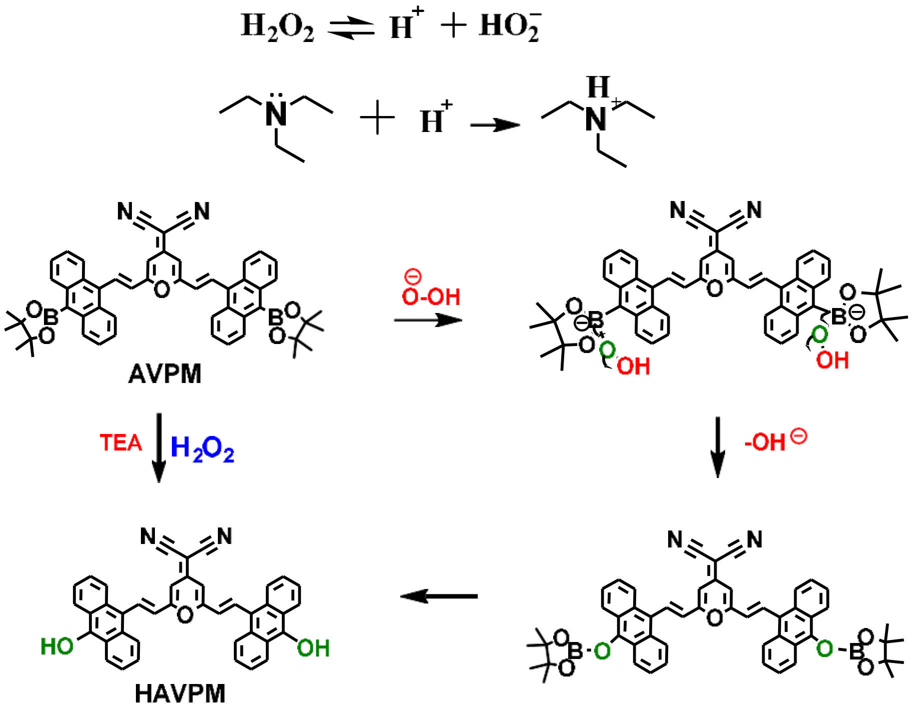
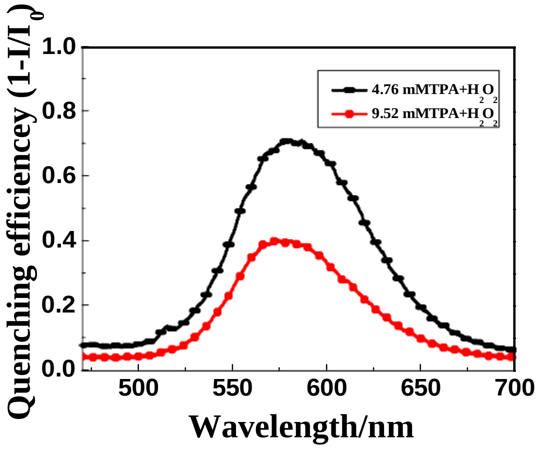


Figure S11. H_2O_2-mediated oxidation of AVPM to give HAVPM.

3 Figures for detailed sensing performance



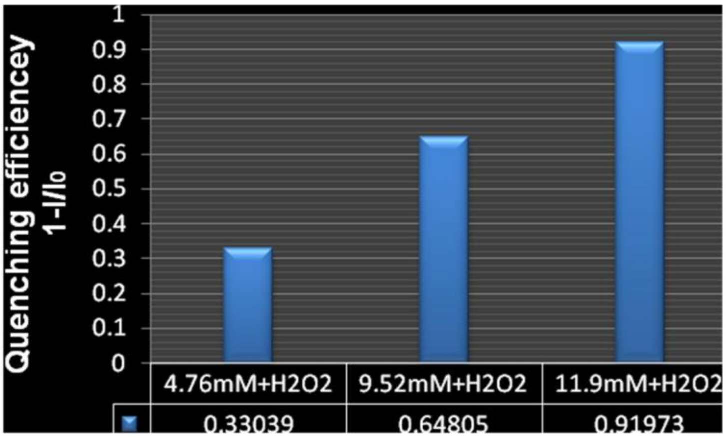
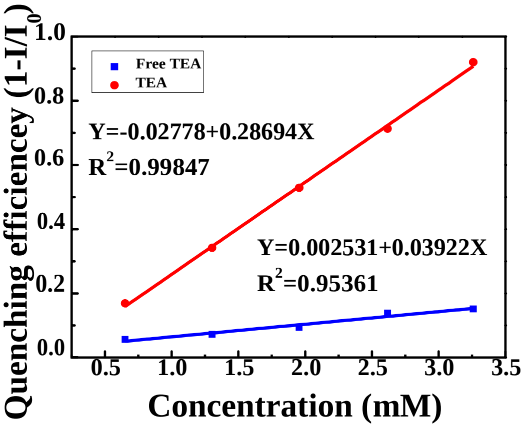
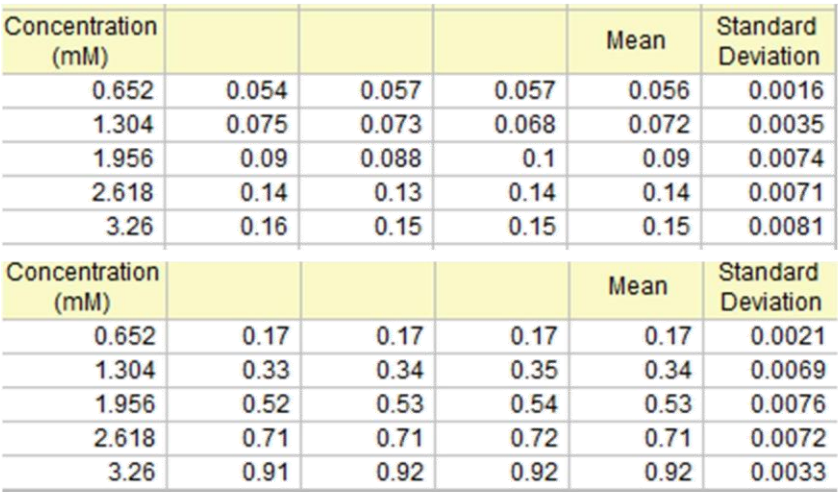


Figure S12. The fluorescence turn-off reaction between AVPM and H_2O_2 was found to be related to the concentration of TEA (4.76 mM; 9.52 mM; 11.9 mM).

4 Detail information about linear fit





Concentration (mM)				Mean	Standard Deviation
0.652	0.054	0.057	0.057	0.056	0.0016
1.304	0.075	0.073	0.068	0.072	0.0035
1.956	0.09	0.088	0.1	0.09	0.0074
2.618	0.14	0.13	0.14	0.14	0.0071
3.26	0.16	0.15	0.15	0.15	0.0081

Concentration (mM)				Mean	Standard Deviation
0.652	0.17	0.17	0.17	0.17	0.0021
1.304	0.33	0.34	0.35	0.34	0.0069
1.956	0.52	0.53	0.54	0.53	0.0076
2.618	0.71	0.71	0.72	0.71	0.0072
3.26	0.91	0.92	0.92	0.92	0.0033

Figure S13. A plot of fluorescence quenching efficiency (1-I/I_0) at 596 nm as a function of H_2O_2 concentration. Red line: linear calibration curve in the presence of TEA (11.9 mM). Blue line: linear calibration curve in the absence of TEA.

5 DMol3 optical absorption spectrum of Anthracene, AVP, and AVPM.

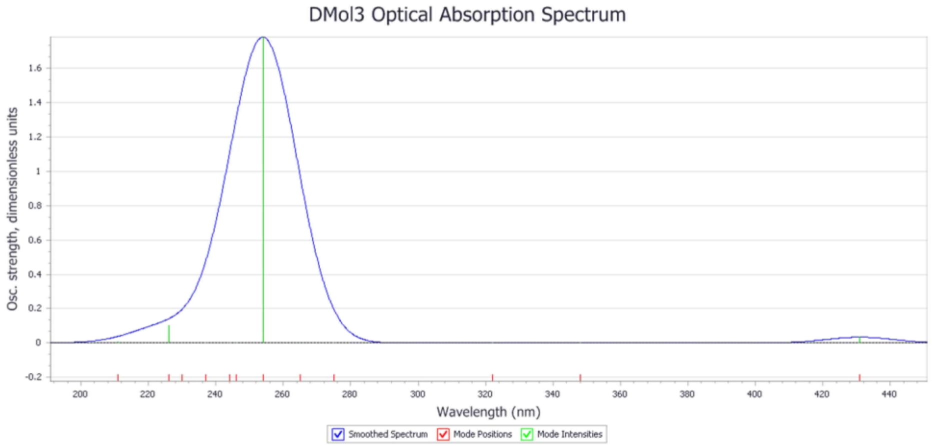


Figure S14. DMol3 optical absorption spectrum of Anthracene.

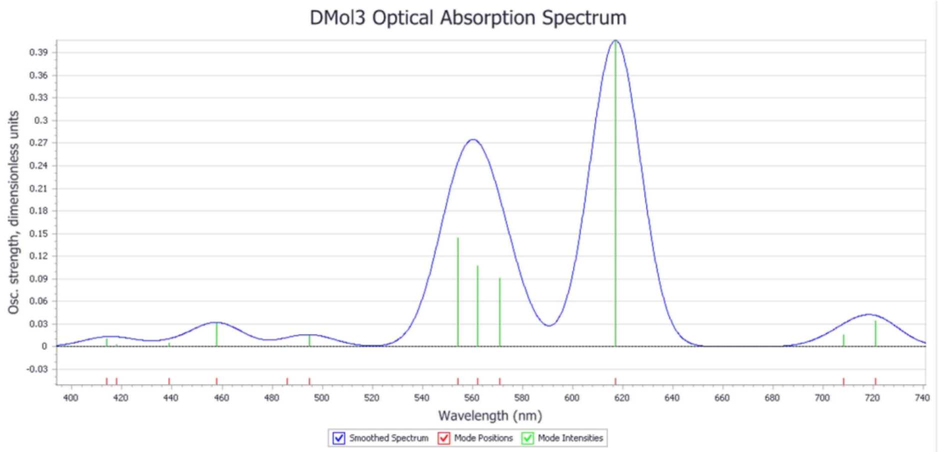


Figure S15. DMol3 optical absorption spectrum of AVP.

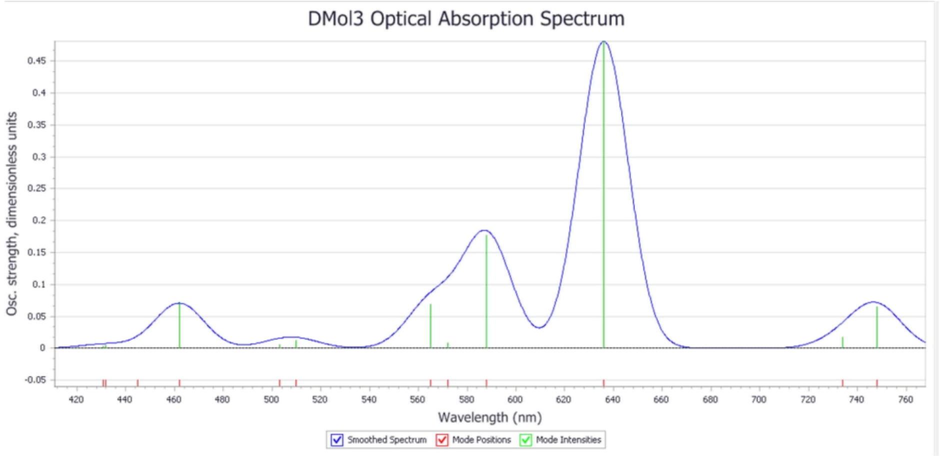


Figure S16. DMol3 optical absorption spectrum of AVPM.

6 The selectivity of fluorescent probe

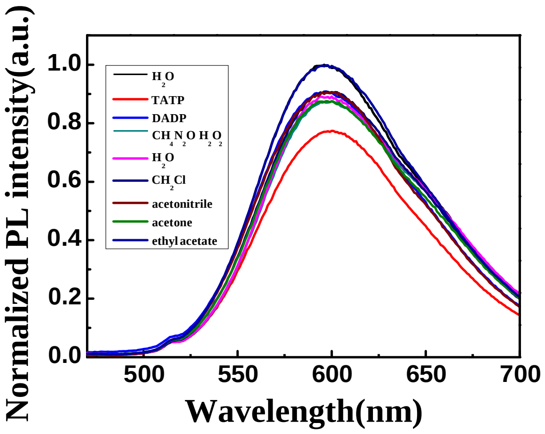


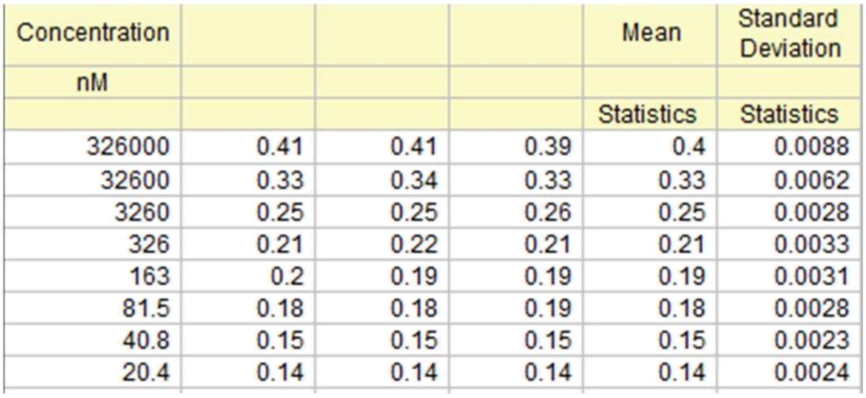
Figure S17. Relative fluorescence intensity at 596 nm of AVPM when in contact with different interferents. (A: H_2O_2; B: TATP; C: DADP; D: $CH_4N_2O{\cdot}H_2O_2$; E: H_2O; F: CH_2Cl_2; G: acetonitrile; H: acetone; I: ethyl acetate).

7 Detection limit measurements

Detection limit measurements of AVPM with respect to H_2O_2 were performed based on the previous literature.[1-3] Fluorescence quenching efficiency ($1\text{-}I/I_0$) were plotted against the concentrations to obtain a linear plot, and the gradient (k) of the plot was then obtained. The maximum emission intensity of AVPM was measured twenty times, and the standard deviation (δ) of these measurements was obtained. Lastly, detection limit was calculated with the following formula.

$$Detection\ Limit = 3\frac{\delta}{k}$$

Where δ is the standard deviation of blank measurement (the maximum emission intensity of AVPM was measured twenty times), k is the slop between the fluorescence emission intensity versus H_2O_2 concentration.



Concentration				Mean	Standard Deviation
nM					
				Statistics	Statistics
326000	0.41	0.41	0.39	0.4	0.0088
32600	0.33	0.34	0.33	0.33	0.0062
3260	0.25	0.25	0.26	0.25	0.0028
326	0.21	0.22	0.21	0.21	0.0033
163	0.2	0.19	0.19	0.19	0.0031
81.5	0.18	0.18	0.19	0.18	0.0028
40.8	0.15	0.15	0.15	0.15	0.0023
20.4	0.14	0.14	0.14	0.14	0.0024

Figure S18. Fluorescence quenching efficiency (1-I/I$_0$) of AVPM (1×10^{-5} M) upon addition of H_2O_2 with concentrations from 2.04×10^{-8} M to 3.26×10^{-4} M in THF.

8 A summary of chromophoric/flourescent probes for hydrogen peroxide detection.

Table S2: A summary of chromophoric/flourescent probes for hydrogen peroxide detection.

Probe	Practical Application	Time	LOD	References
Ti(IV) oxo complexes	peroxide explosives		ppb(vapor)	[4]
CGP with AuNPs	in pH7.4 and 25℃	0.5 h	20 μM	[5]
PB NPs	in ABTS–H_2O_2 system	10 min	0.031μM	[6]
Pd/$CoFe_2O_4$ composite nanotubes	in acetate buffer solution	10 min	1.68 μM	[7]
HPPtCuDs	in TMB-H_2O_2 system		0.1μM	[8]
PDMS-TEOS-SiO_2NPs biocomposite	in TMB-HRP- H_2O_2 system	15 min	1.3μM	[9]
Ag_2S-MMT nanocomposites	in TMB-H_2O_2 system	1 min	0.19μM	[10]
MnSe-g-C_3N_4	in TMB-H_2O_2 system		1.8μM	[11]
V_2O_5 nanozymes	in TMB-OPD-H_2O_2 system		10 μM	[12]
PF1	in vitro	5 min	100 nM	[13]
CPF1	in solution	20 min		[14]
QCy7	PBS 7.4 [50 μM] solutions	30 min		[15]
fluorescein-and rhodol-based	in biological systems			[16]
naphthalimide-based	in 0.1 M phosphate buffer (0.2% DMSO), pH 7.4	120 min		[17]
TPE-BO	In methanol solution		0.52 μM	[18]
Mito-H_2O_2	in DMSO/phosphate buffer (1:99 v/v, 20 mM, pH 7.4)	5 min	0.04 μM	[19]
ABA-HP	In 50% HEPES/DMSO,pH 7.4	30 min	1μM	[20]
Lyso-HP	in live tissue	20 min	1.21μM	[20]
boronobenzo[b]-uinolizinium derivatives	in phosphate buffer (0.1M, pH = 7.4)	140 min	3.0 μM	[21]
AVPM	in THF solution	2 min	17.58 nM	This work

Reference

1. L. L. Long, L. P. Zhou, L. Wang, S. C. Meng, A. H. Gong, F. Y. Du and C. Zhang, *Org.Biomol. Chem.*, 2013, **11**, 8214-8220.
2. C. Y. Ang, S. Y. Tan, S. Wu, Q. Qu, M. F. E. Wong, Z. Luo, P.-Z. Li, S. Tamil Selvan and Y. Zhao, *J. Mater. Chem. C*, 2016, **4**, 2761-2774.
3. J. Xu, Q. Li, Y. Yue, Y. Guo and S. J. Shao, *Biosens. Bioelectron.*, 2014, **56**, 58-63.
4. M. Xu, B. R. Bunes and L. Zang, *ACS Appl. Mater. Interfaces.*, 2011, **3**, 642-647.
5. C. Li, J. Hu, T. Liu and S. Liu, *Macromolecules*, 2011, **44**, 429-431.
6. W. M. Zhang, D. Ma and J. X. Du, *Talanta*, 2014, **120**, 362-367.
7. Z. Yang, Z. Zhang, Y. Jiang, M. Chi, G. Nie, X. Lu and C. Wang, *RSC Adv.*, 2016, **6**, 33636-33642.
8. Y. Lu, W. Ye, Q. Yang, J. Yu, Q. Wang, P. Zhou, C. Wang, D. Xue and S. Zhao, *Sens. Actuators, B*, 2016, **230**, 721-730.
9. J. Pla-Tolós, Y. Moliner-Martinez, C. Molins-Legua and P. Campins-Falcó, *Sens. Actuators, B*, 2016, **231**, 837-846.
10. Q. Y. Liu, Y. L. Jiang, L. Y. Zhang, X. P. Zhou, X. T. Lv, Y. Y. Ding, L. F. Sun, P. P. Chen and H. L. Yin, *Mater Sci Eng C* 2016, **65**, 109-115.
11. F. Qiao, Q. Qi, Z. Wang, K. Xu and S. Ai, *Sens. Actuators, B*, 2016, **229**, 379-386.
12. J. Sun, C. Li, Y. Qi, S. Guo and X. Liang, *Sensors (Basel)*, 2016, **16**.
13. M. C. Y. Chang, A. Pralle, E. Y. Isacoff and C. J. Chang, *J. Am. Chem. Soc.*, 2004, **126**, 15392-15393.
14. M. S. Purdey, J. G. Thompson, T. M. Monro, A. D. Abell and E. P. Schartner, *Sensors (Basel)*, 2015, **15**, 31904-31913.
15. N. Karton-Lifshin, E. Segal, L. Omer, M. Portnoy, R. Satchi-Fainaro and D. Shabat, *J. Am. Chem. Soc.*, 2011, **133**, 10960-10965.
16. B. C. Dickinson, C. Huynh and C. J. Chang, *J. Am. Chem. Soc.*, 2010, **132**, 5906-5915.
17. W. Sun, Z. Ma, J. Li, W. Li, L. Du and M. Li, *Sci. Chi. Chem.*, 2013, **56**, 1440-1445.
18. W. Zhang, W. Liu, P. Li, F. Huang, H. Wang and B. Tang, *Anal. Chem.*, 2015, **87**, 9825-9828.
19. J. Xu, Y. Zhang, H. Yu, X. Gao and S. Shao, *Anal Chem*, 2016, **88**, 1455-1461.
20. M. Ren, B. Deng, J. Y. Wang, X. Kong, Z. R. Liu, K. Zhou, L. He and W. Lin, *Bios. Bioel.*, 2016, **79**, 237-243.
21. R. Bortolozzi, S. von Gradowski, H. Ihmels, K. Schafer and G. Viola, *Chem. Com. (Camb)*, 2014, **50**, 8242-8245.