Supporting Information

A TD-DFT Study on a Class of D-π-A Fluorescent Probes for Typical Oxidants Detection

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Molecular dynamics simulation details

All MD simulations were performed using the GROMACS 2021.3 package[1]. The generalized Amber force field (GAFF)[2] parameters were used to describe bonded and nonbonded interactions for all studied molecules. Restrained electrostatic potential (RESP)[3] charges calculated at the B3LYP/6-311G(d,p) level were used to describe electrostatic properties of all studied molecules. Gaussian 09 was used to optimize molecular structure and obtain wave function. RESP charges were calculated by Multiwfn. Water molecules were modelled with the SPC/E[4] model. Prior to the MD simulations, energy minimization was conducted using the steepest descent method for all the below-explained simulation systems with a truncation force of 100 $kJ \cdot mol^{-1} \cdot nm^{-1}$. 1 ns NPT(P = 1.01325 kpa and T = 298.15 K) equilibrium phase simulation with a Velocity-rescale thermostat[5] and Berendsen barostat[6] with the time constants of couplings being 0.2 and 0.5 ps, respectively. Long-range electrostatic interactions were handled by the Particle-mesh Ewald (PME)[7] method with a cut-off of 1.0 nm used (for electrostatic and Lennard-Jones interactions). Finally, 200 ns NPT simulation with a Velocity-rescale thermostat and Parrinello-Rahman barostat[8] with the time constants of couplings being 0.2 and 2.0 ps of production of MD simulation was performed to obtain the final equilibrium state. When calculating the interaction between molecules, the electrostatic and Lennard-Jones interactions was calculated by setting with a cut-off of 2.5 nm. Periodic boundary conditions were applied in all three dimensions.

Precisely, the simulations were executed in four groups. In order to simulate and calculate the interaction between four types of probes and MnO_4^- more consistently with the real solvent environment, we modeled the interaction according to the experimental conditions. The initial configuration of probe and solvent molecule were randomly placed in a 6 × 6 × 6 nm cube by Packmol[9] software. Then, the system includes 1 probe, 32 MnO_4^-, 32 K^+, 250 THF, 225 water and 1420 DMSO molecules.

Experimental details

Preparation of the CDMA-DM probe: 0.018 g (0.25 mmol) sodium ethoxide was dissolved with 10 mL ethanol in a 25 mL round-bottom flask with a reflux condensing tube under continuous magnetically stirring. Subsequently, 0.726 g (11 mmol) malononitrile and 0.51 g (5 mmol) 3-hydroxy-3-methyl-2-Butanone were added into the flask, and the obtained mixture solution was heated up to at 90 °C and stirred for 5 h. Then, the solution was cooled in a refrigerator until the visible formation of yellowish precipitates, which were filtered out by washing with cold ethanol and then dried overnight with vacuum pumping. Finally, the TCF as the basic raw material for the synthesis of CDMA-DM probe was obtained with a yield of 74%.

0.2 g (1 mmol) TCF and 0.14 g (0.9 mmol) 4-dimethylaminobenzaldehyde were dissolved with 10 mL of ethanol in a 25 mL round-bottom flask with a reflux condensing tube, the oil bath was kept at 90 °C and the mixture was kept stirred for 6 h, the temperature of the mixture solution was maintained around 70-75 °C due to the reflux condensation. After cooling and filtering procedure, the precipitate products were then purified through the column chromatography, then the desired probe (E)-2-(3-cyano-4-(4-(dimethylamino)styryl)-5,5-dimethylfuran-2(5H)-ylidene) malononitrile (CDMA-DM) was obtained with a yield of 56%.

Preparation of the probe solution (8 μM): 3.3 mg CDMA-DM was dissolved in 20 mL THF/DMSO solution with a

volume ratio of 5:25 to obtain the stock CDMA-DM probe solution with a concentration of 0.5 mM. Then, 320 μL stock solution was mixed with 19680 μL THF/DMSO solution to obtain the prepared probe solution (8 μM).

Preparation of the $KMnO_4$ solution (12 mM): 18.96 mg $KMnO_4$ solid was dissolved in 10 mL deionized water to obtain the stock $KMnO_4$ solution with a concentration of 12 mM. Then the solution was diluted with deionized water to obtain various concentrations of $KMnO_4$ solutions for the following experiment.

Preparation of analyte stock solution (25 mM): $NaClO_2$, $NaClO_3$, $NaClO_4$, $NaIO_4$, KI, H_2O_2, $NaC_2H_3O_2$ (sodium acetate, CH_3COONa) and ZnO were dissolved in deionized water to prepare the analyte stock solution with a concentration of 25 mM.

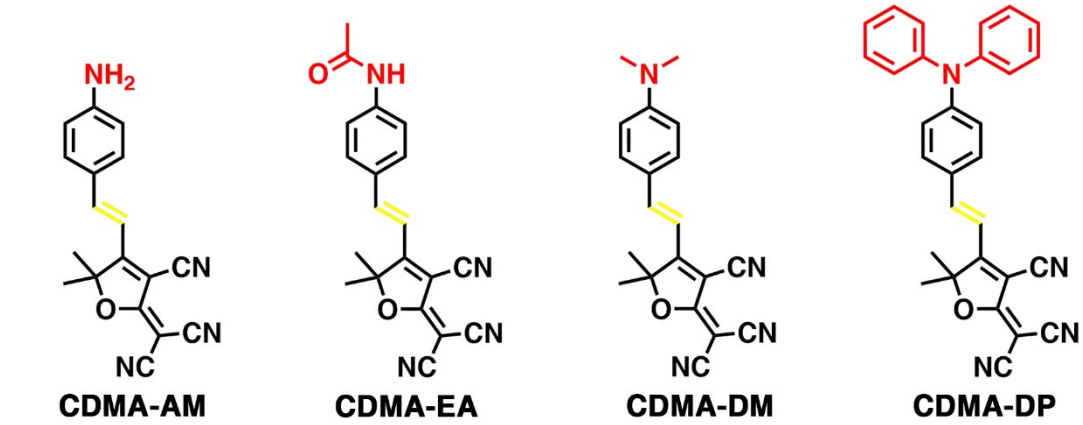
Selectivity testing procedures: $KMnO_4$ solution (6 mM, 75 μL) and the analyte stock solution (25 mM, 180 μL) were added into the colorimetric dishes containing 2925 μL and 2820 μL CDMA-DM probe solutions, respectively. The actual concentrations of $KMnO_4$ solution and the analyte stock solution were 150 μM and 1.5 mM, respectively. After the reaction, the fluorescence spectra were measured and recorded.

Anti-interference testing procedures: By adding KMnO4 solution (6 mM, 75 μL) and the analyte stock solution (25 mM, 180 μL) into a colorimetric dish containing 2745 μL CDMA-DM probe solution, the ratio of the KMnO4 solution to the actual concentration of the analyte was kept as 1:10. Then the fluorescence spectra were measured and recorded after the reaction.

Preparation of the polyacrylic acid (PAA) hydrogel: 1.4 g acrylic acid, 20 mg acrylamide and 200 μL ammonium persulfate solution (25 g/L) were mixed with 10 mL deionized water, and then the obtained mixture solution was magnetic stirred for 10 min to obtain the PAA gel aqueous solution. The PAA gel aqueous solution was then poured into the sealed glass mold and heated at 65 °C for 6 h to obtain the raw PAA hydrogel. The raw PAA hydrogel was then soaked in deionized water for preservation. The water content (WC) of the final prepared PAA hydrogel is 99.79%.

Preparation of the hydrogel chip: First, the prepared PAA hydrogel (a round cake with a diameter of 10 mm and a thickness of 1 mm) was soaked in 10 mL THF/DMSO solution with a volume ratio of 5:25 for 5 cycles. Then, the hydrogel was immersed in the prepared CDMA-DM probe solution (10 mL, 8 μM) with same procedure to obtain the desired hydrogel chip.

Preparation of the filter paper chip: The filter paper was immersed into the prepared CDMA-DM probe solution (10 mL, 8 μM) for 1 min. After sufficient infiltration, the soaked filter paper was removed and dried naturally in air, then the desired filter paper chip was obtained and stored at room temperature for the latter use.



Scheme S1 Probe structure formula of different electron donor modified groups.

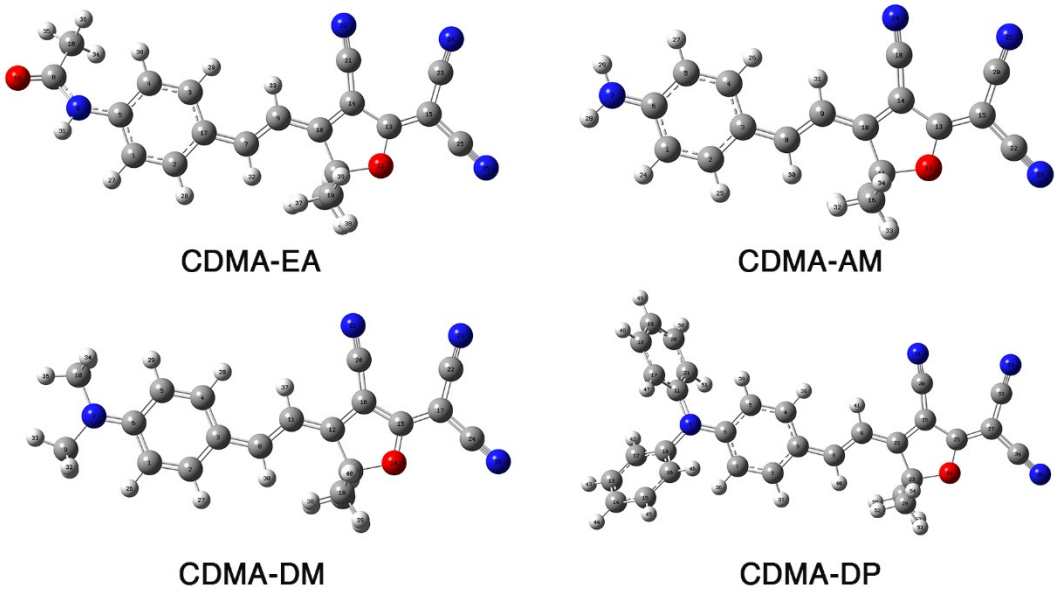


Fig. S1 Ground state geometry optimized structure of CDMA-EA, CDMA-AM, CDMA-DM, CDMA-DP.

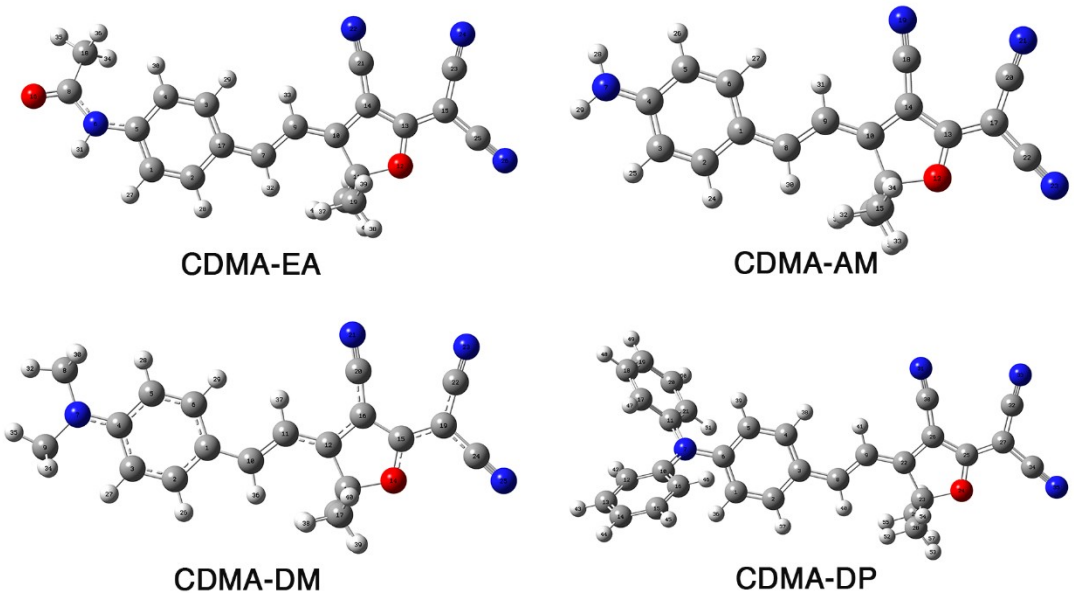


Fig. S2 Excited state geometry optimized structure of CDMA-EA, CDMA-AM, CDMA-DM, CDMA-DP.

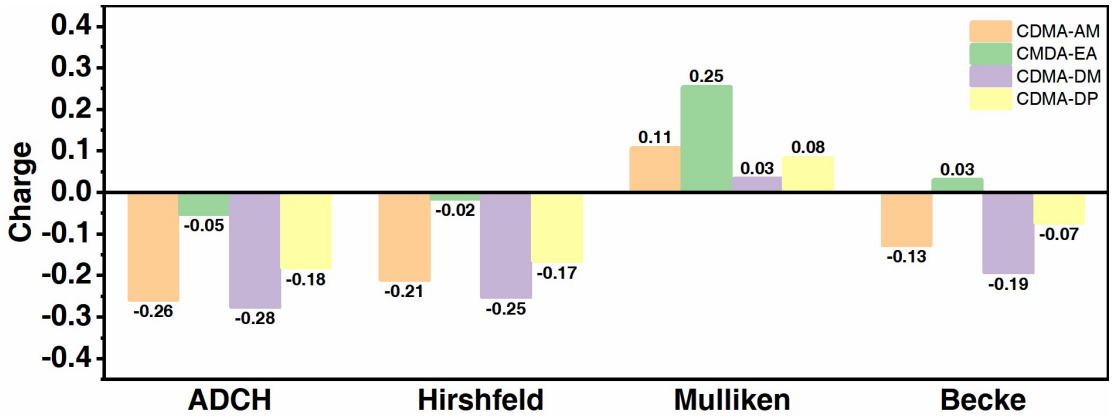


Fig. S3 Comparison of the total charge of the π-conjugated bridge together with the EWG analyzed through different methods.

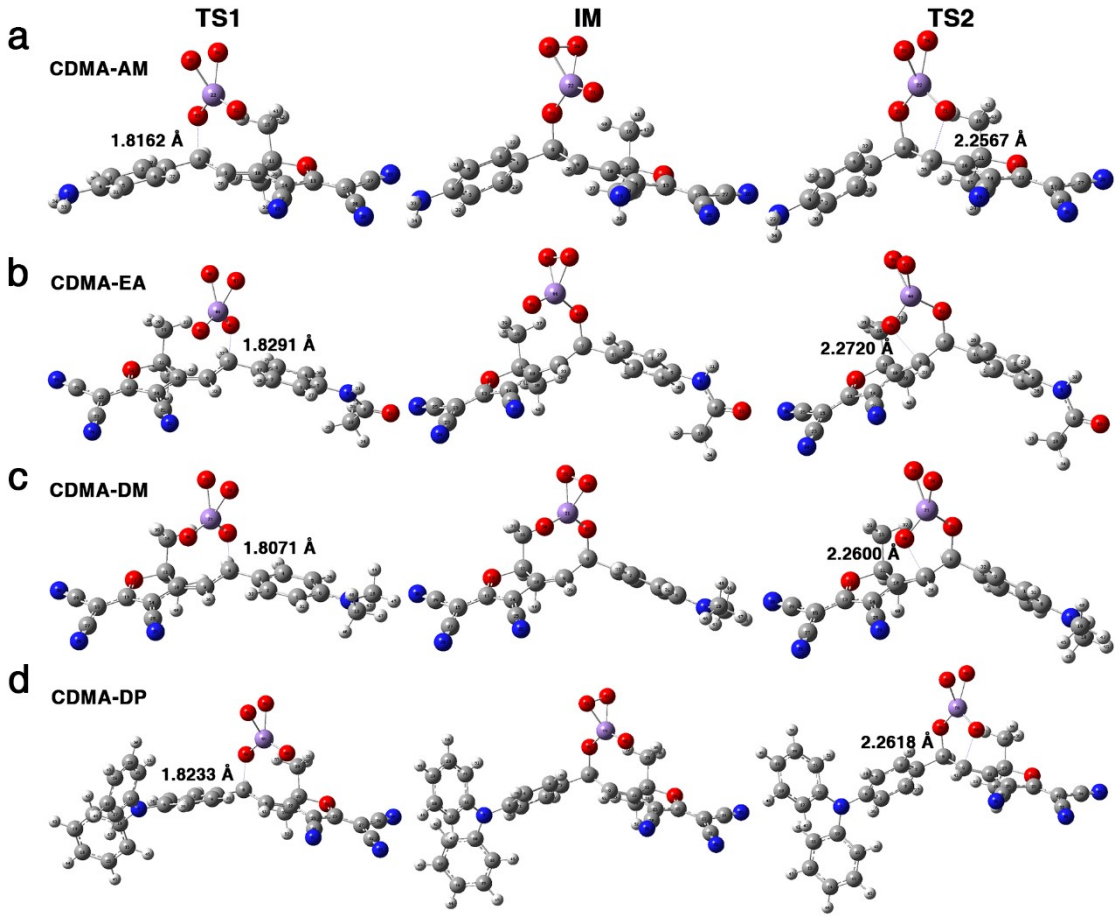


Fig. S4 Overall structure of the TS1, TS2 and IM states in CDMA-AM, CDMA-EA, CDMA-DM and CDMA-DP probes.

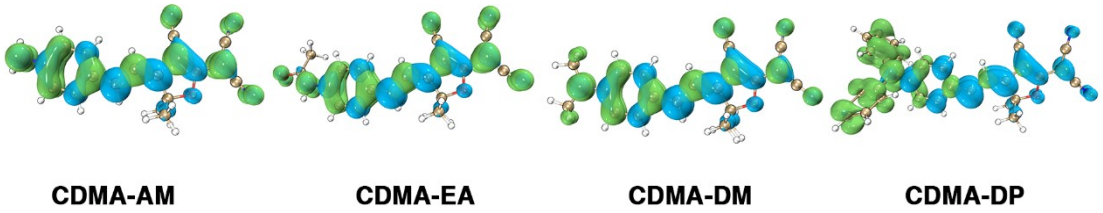


Fig. S5 Electron-hole distribution in the probes.

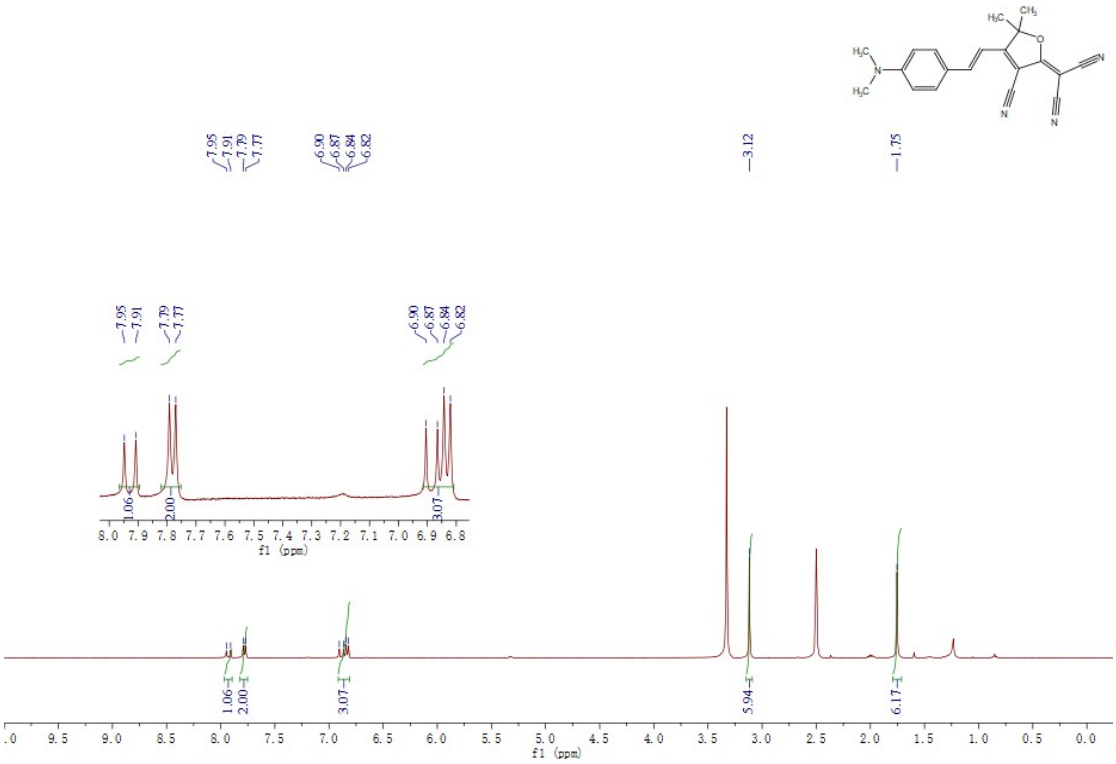


Fig. S6 ^{1}H NMR spectrum of CDMA-DM (400 MHz, DMSO-d_6) δ 7.93 (d, J = 15.8 Hz, 1H), 7.78 (d, J = 8.9 Hz, 2H), 6.91-6.81 (m, 3H), 3.12 (s, 6H), 1.75 (s, 6H).

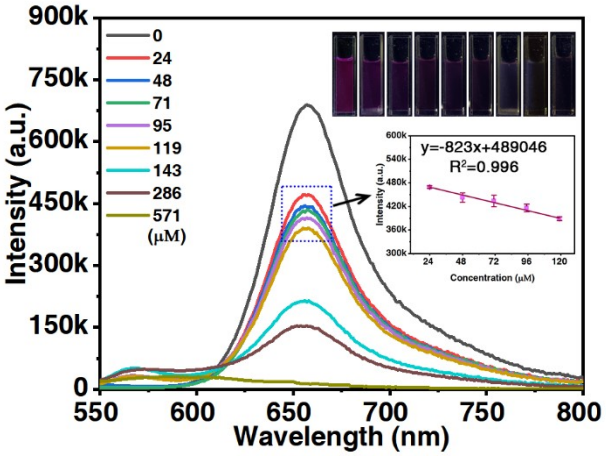


Fig. S7 Fluorescence emission spectra and images obtained in response to different concentrations of $KMnO_4$ (inset: the linear fitting of the fluorescence response intensities at 657 nm towards 24-120 μM $KMnO_4$).

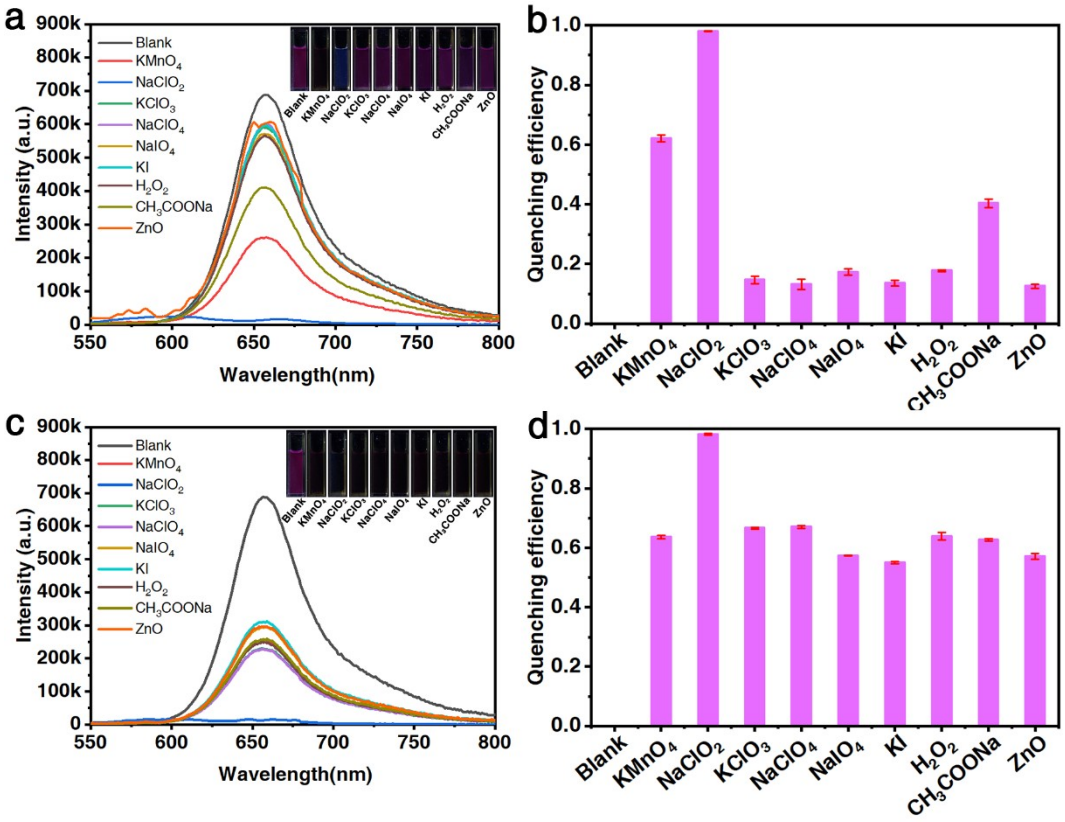


Fig. S8 (a) The fluorescence spectra and (b) the fluorescence quenching efficiencies at 657 nm obtained for the CDMA-DM probe (8 μM) in response to 1.5 mM various analytes and 0.15 mM $KMnO_4$. (c) The fluorescence spectra and (d) the fluorescence quenching efficiencies at 657 nm obtained for the CDMA-DM probe (8 μM) in response to mixtures of 1.5 mM various analytes and 0.15 mM $KMnO_4$, respectively. (All experiments were repeated for three times).

Table S1 Comparison of the benchmark analysis for the CDMA-DM probe with different basis sets..

Basis Set	Computation Amount (core·s)	Energy (Hartree)	ADCH Charger (12-25,38-43)	ADCH Charger Deviation Standard %
6-31G(d)	1027.10	-1065.91	-0.38873945	-3.41
6-31G(d,p)	1150.30	-1065.93	-0.3881548	-3.56
6-311G(d)	1550.40	-1066.12	-0.3936568	-2.12
6-311G(d,p)	1800.90	-1066.15	-0.39344918	-2.17
cc-pvdz	1837.00	-1065.98	-0.38351186	-4.82
cc-pvtz	11842.90	-1066.25	-0.39747612	-1.14
cc-pvqz	127262.80	-1066.32	-0.40120956	-0.19
def2-qzvpp	145345.90	-1066.34	-0.40199153	0.00

Table S2 Cartesian coordinate xyz for the ground state optimized structure of the CDMA-AM probe molecule.

	X	Y	Z
C	-5.43906400	-0.95578800	0.00084800
C	-4.09626500	-1.23698100	0.00092700
C	-3.11754900	-0.21678700	0.00013400
C	-3.57825300	1.12142500	-0.00082300
C	-4.91519700	1.41831400	-0.00098000
C	-5.88640100	0.38540000	-0.00015300
N	-7.19779500	0.67687600	-0.00029200
C	-1.74322200	-0.58178100	0.00028200
C	-0.66066200	0.26053400	0.00027300
C	0.68498500	-0.14143900	0.00019400
C	1.22941600	-1.55225000	-0.00007600
O	2.67751400	-1.34999500	-0.00018300
C	2.97140900	-0.06065900	-0.00000500
C	1.77505700	0.71777700	0.00024100
C	4.30385500	0.31755100	-0.00008600
C	0.91593400	-2.32259600	1.27196300
C	0.91566500	-2.32217600	-1.27229100
C	1.67858700	2.12349900	0.00044500
N	1.53600000	3.27092100	0.00061200
C	4.71604200	1.66721500	0.00018000
N	5.09075200	2.76222400	0.00041200
C	5.31014000	-0.67526600	-0.00043400
N	6.14223400	-1.47933200	-0.00077300
H	-6.16754500	-1.76051900	0.00154400
H	-3.77436800	-2.27468400	0.00165900
H	-2.86906500	1.94239900	-0.00158000
H	-5.24215100	2.45355300	-0.00180000
H	-7.89400000	-0.04781000	-0.00026100
H	-7.52397300	1.62728900	-0.00134300
H	-1.56341900	-1.65302200	0.00046500
H	-0.82604000	1.33438300	0.00035400
H	-0.14567500	-2.56202500	1.33470000
H	1.48115400	-3.25634800	1.27430000
H	1.19265700	-1.73863900	2.15150600
H	-0.14598700	-2.56143500	-1.33493400
H	1.19232400	-1.73797800	-2.15169500
H	1.48077800	-3.25599200	-1.27500100

Table S3 Cartesian coordinate xyz for the ground state optimized structure of the CDMA-EA probe molecule.

	X	Y	Z
C	4.29491200	-1.64713400	-0.09262200
C	2.92603600	-1.80513900	-0.04509600
C	2.63728500	0.57394700	-0.25851200
C	4.00486900	0.73878600	-0.32142100
C	4.85899200	-0.36974800	-0.21505600
N	6.24480100	-0.27347700	-0.28403400
C	0.64029000	-0.92929500	-0.04630600
C	7.12631500	0.70546400	0.12642500
C	-0.33734500	0.01479800	-0.07060100
C	-1.72965600	-0.24463500	-0.01434700
C	-2.41462400	-1.58745700	0.08266100
O	-3.83267300	-1.23124000	0.09860900
C	-3.99096700	0.07714000	0.02726400
C	-2.71029100	0.72197600	-0.04410500
C	-5.26745600	0.60256700	0.03042200
O	8.31520100	0.53957300	-0.07545000
C	2.06016600	-0.69953700	-0.11237200
C	6.60124900	1.91834200	0.83951200
C	-2.21553600	-2.45934900	-1.14643500
C	-2.15017100	-2.30953800	1.39385100
C	-2.46507100	2.10919500	-0.13285600
N	-2.20691700	3.23279600	-0.20664700
C	-5.52605200	1.98921100	-0.04217300
N	-5.77623900	3.11705000	-0.09966600
C	-6.37892700	-0.26962800	0.10952400
N	-7.29359900	-0.97428800	0.17360700
H	4.94419700	-2.51396700	-0.02196700
H	2.51136600	-2.80332700	0.05770300
H	2.01097400	1.45425400	-0.35206200
H	4.40779600	1.72811300	-0.48955500
H	6.72819100	-1.10185600	-0.60463300
H	0.35862900	-1.97487500	0.03104600
H	-0.06437600	1.06415800	-0.13891900
H	5.73737000	1.70602900	1.47064100
H	7.41225600	2.31551900	1.44799200
H	6.31846000	2.69061600	0.11910700
H	-1.18767300	-2.81592800	-1.21278700
H	-2.87708200	-3.32479000	-1.08035400
H	-2.44974600	-1.90228100	-2.05521000
H	-1.11830900	-2.65587700	1.45098800
H	-2.34371300	-1.64994800	2.24152700
H	-2.80899700	-3.17686500	1.46183900

Table S4 Cartesian coordinate xyz for the ground state optimized structure of the CDMA-DM probe molecule.

	X	Y	Z
C	4.66536000	-1.18560300	-0.00026500
C	3.31406100	-1.42214900	-0.00023700
C	2.36548300	-0.37521400	0.00001600
C	2.87175600	0.94532900	0.00029400
C	4.21706300	1.20177600	0.00028000
C	5.16816500	0.14244900	-0.00003600
N	6.49378700	0.39326300	-0.00010200
C	0.98113700	-0.69652600	-0.00000700
C	7.44500600	-0.70100000	0.00000700
C	6.98452400	1.75797000	-0.00001700
C	-0.07408100	0.18087400	0.00001800
C	-1.43165300	-0.17620200	0.00000900
C	-2.02233700	-1.56816800	0.00007000
O	-3.46347000	-1.31823800	0.00002000
C	-3.71440800	-0.01968800	-0.00001800
C	-2.49350000	0.71862900	-0.00002600
C	-5.03379700	0.40240800	-0.00004800
C	-1.73462200	-2.34826900	-1.27203800
C	-1.73466400	-2.34807800	1.27230500
C	-2.35098500	2.12040300	-0.00006100
N	-2.17072100	3.26257200	-0.00010600
C	-5.40009600	1.76523700	-0.00009400
N	-5.73705500	2.87246700	-0.00012100
C	-6.07260500	-0.55625700	-0.00003300
N	-6.93107500	-1.33215900	0.00003900
H	5.34388300	-2.02868300	-0.00049900
H	2.96233700	-2.45024200	-0.00043800
H	2.19083200	1.78995200	0.00058000
H	4.54946800	2.23176100	0.00057600
H	0.76705000	-1.76157200	-0.00007500
H	7.33092000	-1.32981700	0.88858000
H	7.33130800	-1.32968000	-0.88871600
H	8.45444400	-0.29782600	0.00026200
H	6.65147800	2.30339000	-0.88853600
H	6.65235900	2.30301800	0.88907300
H	8.07150000	1.74669900	-0.00058200
H	0.12661500	1.24878600	0.00002000
H	-0.68093400	-2.62006300	-1.33651300
H	-2.32820400	-3.26425600	-1.27330000
H	-1.99471300	-1.75626000	-2.15128900
H	-0.68093600	-2.61967200	1.33694400
H	-1.99495800	-1.75599500	2.15144700
H	-2.32809600	-3.26416300	1.27361600

Table S5 Cartesian coordinate xyz for the ground state optimized structure of the CDMA-DP probe molecule.

	X	Y	Z
C	2.41052300	-1.40901200	0.38572600
C	1.04905100	-1.60053500	0.42380600
C	0.14186000	-0.56541800	0.11943600
C	0.68734600	0.68631800	-0.23820700
C	2.04403600	0.89042400	-0.27996000
C	2.94392700	-0.15296400	0.03458900
N	4.30603300	0.05593300	-0.00668400
C	-1.25970900	-0.83300400	0.18700100
C	-2.27667000	0.05398200	-0.03150900
C	5.21670200	-1.02570500	-0.15866100
C	4.85832700	1.36031600	0.11916800
C	6.29571500	-1.14725200	0.71589600
C	7.20380900	-2.18536800	0.55363200
C	7.03726900	-3.11038500	-0.47254300
C	5.95928700	-2.98657700	-1.34412000
C	5.05446600	-1.94348400	-1.19646100
C	5.80819400	1.79914500	-0.80237200
C	6.37143300	3.06125200	-0.66665400
C	5.98583300	3.89397300	0.37959700
C	5.03787000	3.45318600	1.29817300
C	4.48016400	2.18712900	1.17700700
C	-3.65176800	-0.24521600	0.03963100
C	-4.29254800	-1.57797100	0.35297000
O	-5.72280900	-1.28218100	0.28070100
C	-5.92561100	-0.01136800	-0.01975200
C	-4.67386700	0.66273800	-0.17634900
C	-7.22499100	0.44976000	-0.13197400
C	-4.03073700	-2.63792600	-0.70454100
C	-4.03689000	-2.05697800	1.77272200
C	-4.47861100	2.02225900	-0.49485500
N	-4.25841700	3.12724100	-0.75287700
C	-7.53657800	1.78893700	-0.45153400
N	-7.82892200	2.87781500	-0.71186500
C	-8.30138100	-0.44334000	0.07651800
N	-9.18871000	-1.16624900	0.24490100
H	3.07613400	-2.22395000	0.64335200
H	0.66338600	-2.57385300	0.71325700
H	0.03607500	1.51092700	-0.50746000
H	2.43083200	1.85808400	-0.57634900
H	-1.50944900	-1.85778000	0.44554200
H	-2.03702800	1.08446000	-0.27910200
H	6.41758400	-0.42619700	1.51761300

H	8.04099300	-2.27532000	1.23835100
H	7.74647600	-3.92246400	-0.59489700
H	5.82814300	-3.69718700	-2.15383200
H	4.22153300	-1.83322900	-1.88324700
H	6.10058000	1.14781600	-1.61959400
H	7.10922500	3.39796800	-1.38784000
H	6.42494400	4.88106000	0.48088600
H	4.73965000	4.09171900	2.12348700
H	3.75316100	1.83243400	1.90040400
H	-2.98811400	-2.95588300	-0.69212900
H	-4.65938800	-3.50715900	-0.50345000
H	-4.26468300	-2.25396600	-1.69903100
H	-2.99646600	-2.35307200	1.90667000
H	-4.26954100	-1.26959100	2.49176000
H	-4.67017700	-2.92202900	1.97738400

Table S6 The energy, the number of virtual frequencies and the frequency of virtual frequencies after probe structure optimization.

	Energy (a.u.)	Virtual frequency number	Virtual frequency ratio (cm^{-1})
CDMA-AM			
OPT	-987.6169	/	/
TS1	-2440.1697	1	-463.08
TS2	-2440.1587	1	-557.54
CDMA-EA			
OPT	-1140.1403	/	/
TS1	-2592.8110	1	-478.94
TS2	-2592.8061	1	-531.98
CDMA-DM			
OPT	-1066.1462	/	/
TS1	-2518.7567	1	-458.95
TS2	-2518.7481	1	-551.02
CDMA-DP			
OPT	-1449.2598	/	/
TS1	-2902.1835	1	-474.43
TS2	-2902.1774	1	-546.63

Table S7 Cartesian coordinate xyz of CDMA-AM probe molecule and MnO_4 in TS1 state.

	X	Y	Z
C	2.67031200	-1.00671300	0.39142300
C	3.55532700	-1.32709600	1.42686900
C	4.81721900	-1.83154700	1.16486400
C	5.24483700	-2.01439400	-0.15946600
C	4.36688100	-1.67258600	-1.20416000
C	3.10515800	-1.18143800	-0.92942400
N	6.51971300	-2.46314400	-0.43393600
C	1.33803200	-0.48140900	0.71961900
C	0.22180900	-0.75982900	-0.12204600
C	-1.09214700	-0.64154500	0.24921300
C	-1.65342000	-0.29315100	1.61955100
O	-3.10035600	-0.29155300	1.40280300
C	-3.38923600	-0.62613700	0.14627700
C	-2.21352800	-0.84971400	-0.59306600
C	-1.38884200	-1.37721000	2.65837700
C	-1.29079600	1.10565000	2.09706100
C	-4.73524100	-0.69236900	-0.21323500
C	-2.11009100	-1.17600800	-1.96085100
N	-1.94724600	-1.43935900	-3.07343200
C	-5.14975700	-1.05539200	-1.51505100
O	0.24068500	2.13258600	-1.55397700
Mn	1.21275400	2.44421000	-0.41755700
O	1.66732900	1.30336000	0.65054900
O	1.25647100	4.12098300	0.14891700
O	2.34438800	3.78094800	-0.68211900
N	-5.51498200	-1.35211800	-2.56999400
C	-5.73354900	-0.40006200	0.74646900
N	-6.55300000	-0.16325000	1.52541500
H	3.24317000	-1.18655000	2.45652300
H	5.48434900	-2.08510100	1.98102600
H	4.69037000	-1.79624300	-2.23159900
H	2.45792800	-0.91673200	-1.75787200
H	6.67428200	-2.85964200	-1.34922100
H	6.99260200	-2.96400300	0.30386000
H	1.14825000	-0.43743700	1.78584500
H	0.41581000	-1.04232000	-1.15065800
H	-0.33023600	-1.42701500	2.91145600
H	-1.95279000	-1.14861000	3.56403000
H	-1.70358700	-2.34923900	2.27546500
H	-0.22992100	1.16927400	2.33754400
H	-1.51409800	1.84082200	1.32144000
H	-1.87229900	1.33775000	2.99080100

Table S8 Cartesian coordinate xyz of CDMA-AM probe molecule and MnO_4 in TS2 state.

	X	Y	Z
C	-2.73338500	-0.79488900	-0.44831200
C	-3.24660500	-1.74542700	-1.32643500
C	-4.38425100	-2.47871600	-1.00719800
C	-5.04264900	-2.27131000	0.20944900
C	-4.53006400	-1.30966400	1.09326800
C	-3.39323200	-0.58801200	0.76528800
N	-6.21935400	-2.95512100	0.51147400
C	-1.48884600	-0.01199100	-0.78772900
C	-0.36180100	-0.31357200	0.13002900
C	0.96347900	-0.44927700	-0.23339000
C	1.57736800	-0.22089500	-1.60331300
O	3.01261400	-0.35916700	-1.35327600
C	3.23781300	-0.71635000	-0.09176000
C	2.02378500	-0.79241200	0.62780400
C	1.22816100	-1.32003800	-2.60277800
C	1.35596000	1.18291600	-2.14549100
C	4.55365600	-0.94016300	0.29963300
C	1.85989700	-1.08562000	1.99882700
N	1.65701000	-1.31505400	3.11167000
C	4.89264500	-1.33670000	1.61475000
O	0.02402900	1.76901000	0.90902500
Mn	-1.09189300	2.63471500	0.24510800
O	-1.83242400	1.42162700	-0.74717100
O	-0.92522700	4.39736300	0.04407500
O	-1.80701400	4.02834900	1.08150600
N	5.19572500	-1.66422600	2.67960900
C	5.60184800	-0.78034400	-0.63959800
N	6.45995900	-0.65155400	-1.40128100
H	-2.75244900	-1.92250800	-2.27666800
H	-4.76947100	-3.21454600	-1.70484300
H	-5.03325100	-1.13270400	2.03787100
H	-3.01692700	0.15496500	1.46204700
H	-6.42439800	-3.03378700	1.49790200
H	-6.32964100	-3.84182300	0.03939300
H	-1.22137400	-0.20314900	-1.82702100
H	-0.62064300	-0.60798900	1.14210200
H	0.18091900	-1.26720000	-2.89711400
H	1.84533200	-1.19451600	-3.49375500
H	1.42310300	-2.30132800	-2.16732000
H	0.29986300	1.34016300	-2.36857500
H	1.67108400	1.92539200	-1.41097100
H	1.93330900	1.31018100	-3.06260600

Table S9 Cartesian coordinate xyz of CDMA-EA probe molecule and MnO_4 in TS1 state.

	X	Y	Z
C	3.88151400	-0.30721500	1.28060200
C	2.54900700	-0.08527800	0.98030600
C	3.02170600	-0.41188900	-1.35574900
C	4.36263500	-0.62511100	-1.06340900
C	4.79641600	-0.59458800	0.26129800
N	6.15074700	-0.78606600	0.60816400
C	0.67753600	0.05092300	-0.69290400
C	7.04902300	-1.71695500	0.15565100
C	-0.33735400	-0.46120400	0.15041600
C	-1.65088100	-0.64990400	-0.22125300
C	-2.27116300	-0.45186500	-1.59527700
O	-3.67966100	-0.78216900	-1.37984300
C	-3.88800900	-1.16114100	-0.12217800
C	-2.68867000	-1.09817000	0.62085500
C	-5.17815400	-1.53307100	0.24178600
O	8.19396900	-1.70307700	0.58113400
C	2.09880700	-0.15434400	-0.34222800
C	6.58997200	-2.75144000	-0.84056500
C	-2.23969100	0.98950800	-2.08295300
C	-1.76054300	-1.45435200	-2.62441400
C	-2.51545800	-1.38246100	1.99236600
N	-2.30192400	-1.59413000	3.10677700
C	-5.49698600	-1.96987000	1.54897800
N	-5.78354800	-2.33343000	2.60677300
C	-6.21842300	-1.48638000	-0.71837700
N	-7.07053800	-1.44927300	-1.49665200
H	4.22462300	-0.26416400	2.30779000
H	1.85813000	0.14973700	1.78180700
H	2.69292600	-0.43492100	-2.38882100
H	5.06911800	-0.78734100	-1.86636700
H	6.50607600	-0.22484100	1.37344300
H	0.49315000	0.04378600	-1.76053100
H	-0.08292300	-0.68371900	1.18087600
H	7.20894800	-3.63515100	-0.70026300
H	5.53757200	-3.00709700	-0.72778600
H	6.75197600	-2.38071300	-1.85474200
H	-1.21925400	1.29983400	-2.30719900
H	-2.84313900	1.07156900	-2.98828000
H	-2.64510200	1.65612700	-1.31902700
H	-1.84441000	-2.46986000	-2.23451800
H	-2.35949200	-1.36766700	-3.53215400
H	-0.71839300	-1.26155600	-2.87631000
O	0.63728300	1.87912300	-0.65087000
Mn	-0.13286100	2.90497700	0.34915800
O	-1.01068300	2.38762400	1.48800200
O	-0.56482600	4.48296800	-0.32491100
O	0.55402400	4.52811600	0.53273800

Table S10 Cartesian coordinate xyz of CDMA-EA probe molecule and MnO_4 in TS2 state.

	X	Y	Z
C	4.11917200	0.48392700	0.89964200
C	2.82572800	0.91752000	0.64633000
C	2.80204300	-0.33963200	-1.40023400
C	4.10692300	-0.75971100	-1.16583300
C	4.76353000	-0.36600900	-0.00215000
N	6.09595100	-0.76776000	0.26723900
C	0.71705000	0.91444100	-0.74457300
C	6.64334200	-2.01884300	0.22061900
C	-0.21618400	0.18902300	0.15353200
C	-1.39499700	-0.42279400	-0.21925600
C	-2.06447000	-0.39713300	-1.58263800
O	-3.33217300	-1.08783200	-1.34430400
C	-3.39987700	-1.53118300	-0.09167100
C	-2.24231300	-1.16177300	0.62952000
C	-4.53358200	-2.24116100	0.28936500
O	7.82903300	-2.17451400	0.47813400
C	2.14965700	0.49758100	-0.49972800
C	5.75520200	-3.18494800	-0.13638500
C	-2.41288900	1.00412500	-2.06395600
C	-1.33051600	-1.23155600	-2.62761700
C	-1.96514900	-1.40850300	1.99128000
N	-1.67423100	-1.57215600	3.09618300
C	-4.69497200	-2.76221700	1.59476500
N	-4.85097500	-3.20014500	2.65163700
C	-5.57020000	-2.46234900	-0.65032600
N	-6.41750600	-2.64390800	-1.41332300
H	4.63709300	0.79722000	1.79900300
H	2.33413600	1.58419600	1.34634600
H	2.29660500	-0.65787300	-2.30589800
H	4.61710900	-1.37594300	-1.89522400
H	6.72524900	-0.05981900	0.62638900
H	0.47765900	0.74306700	-1.79450200
H	0.13674500	0.00001300	1.16326400
H	6.16917500	-4.07017700	0.34208200
H	4.72163800	-3.03742900	0.17273400
H	5.77510200	-3.34155600	-1.21691900
H	-1.50520100	1.57097100	-2.27698100
H	-3.00283500	0.93242800	-2.97907000
H	-2.98547300	1.53391900	-1.30206300
H	-1.10894900	-2.22425800	-2.23273600
H	-1.96592200	-1.32988000	-3.50915200
H	-0.39833100	-0.75412600	-2.92670100
O	0.61855300	2.36144100	-0.54896700
Mn	-0.62394200	3.20167200	0.33951600
O	-1.41354000	1.97617100	0.88466700
O	-1.46868900	4.71485800	-0.02154500
O	-0.70104600	4.78767700	1.15767200

Table S11 Cartesian coordinate xyz of CDMA-DM probe molecule and MnO_4 in TS1 state.

	X	Y	Z
C	-4.01957500	-1.09109900	-1.03161900
C	-2.70549500	-0.74107700	-0.79605800
C	-2.22152300	-0.54728300	0.50499600
C	-3.12384800	-0.69931100	1.56407900
C	-4.44095500	-1.06148500	1.35341000
C	-4.92877300	-1.27451100	0.04157900
N	-6.22272700	-1.63884200	-0.18377400
C	-0.83672800	-0.15827800	0.78588100
C	0.22752900	-0.59045600	-0.06542500
C	1.55072000	-0.61388400	0.27987100
C	2.17745400	-0.28153600	1.62593200
O	3.60998400	-0.45812300	1.38683300
C	3.83191400	-0.87520400	0.14060700
C	2.62606600	-0.98559500	-0.57151400
C	5.15522600	-1.11756400	-0.23249800
C	1.98969800	1.16753000	2.05127100
C	1.81055600	-1.28552600	2.71294800
C	-7.15106800	-1.74027800	0.92958400
C	-6.71548700	-1.76621900	-1.54519800
O	0.51758400	2.24605600	-1.59896000
Mn	-0.42401400	2.68357500	-0.47873100
O	-0.95871600	1.63958800	0.65041800
O	-0.35529600	4.38911000	-0.00877700
O	-1.46546700	4.07545200	-0.81986600
C	2.45924400	-1.35298000	-1.92207100
N	2.24742800	-1.64111200	-3.02041100
C	5.50019900	-1.58235700	-1.52164900
N	5.80702000	-1.96571000	-2.56740000
C	6.19695700	-0.90975400	0.70204800
N	7.05151600	-0.74268600	1.46141000
H	-4.34871500	-1.22064300	-2.05296500
H	-2.05123200	-0.59848200	-1.64890700
H	-2.78095400	-0.53479500	2.58066100
H	-5.09487400	-1.17494300	2.20641500
H	-0.61807300	-0.10030000	1.84609400
H	-0.01903800	-0.88353100	-1.07981400
H	0.94837800	1.36352800	2.30570300
H	2.61255100	1.36542500	2.92522600
H	2.28060100	1.84065700	1.24227500
H	2.00274100	-2.30191800	2.36573800
H	2.41544800	-1.08896300	3.59956400
H	0.75878100	-1.20193300	2.98456200
H	-6.81452800	-2.48533600	1.65593200
H	-7.26874000	-0.78137400	1.44586800
H	-8.12230700	-2.04987300	0.55260500
H	-6.15799500	-2.52852700	-2.09650400
H	-7.75986500	-2.06573600	-1.51588900
H	-6.64188000	-0.81962800	-2.09130700

Table S12 Cartesian coordinate xyz of CDMA-DM probe molecule and MnO_4 in TS2 state.

	X	Y	Z
C	4.25068900	-0.32097100	0.87913200
C	2.99962000	0.21522700	0.61845100
C	2.33119900	-0.04379000	-0.57850900
C	2.95940000	-0.86309200	-1.51073700
C	4.21174300	-1.41489000	-1.26713100
C	4.89811300	-1.14726000	-0.06628100
N	6.16064800	-1.66075000	0.17319100
C	0.95484200	0.51725200	-0.83365400
C	-0.06103900	-0.04759100	0.08978400
C	-1.33968700	-0.43908000	-0.25191000
C	-2.02942700	-0.28474300	-1.59614600
O	-3.39700200	-0.72829300	-1.32244000
C	-3.50627900	-1.17270900	-0.07305100
C	-2.28093800	-1.02869000	0.61519700
C	-4.73798900	-1.67307300	0.33684600
C	-2.12234700	1.15639700	-2.07529500
C	-1.49083700	-1.24350900	-2.65405700
C	6.63667300	-2.73851600	-0.67848600
C	6.67768500	-1.61546100	1.53147200
O	-0.87700000	1.88148100	0.93876100
Mn	0.03103500	2.98242600	0.30990600
O	1.02524200	1.98386400	-0.70230900
O	-0.56193400	4.64010700	0.08295400
O	0.35129200	4.52170500	1.15079300
C	-2.01675600	-1.33827000	1.96669300
N	-1.73321200	-1.56642000	3.06207800
C	-4.95024900	-2.17960000	1.64057300
N	-5.14921500	-2.60133900	2.69684300
C	-5.82608700	-1.68817600	-0.56975500
N	-6.71690500	-1.70220600	-1.30422400
H	4.72433900	-0.09387100	1.82390400
H	2.53498600	0.85165800	1.36576600
H	2.46249100	-1.08860300	-2.44951100
H	4.65112300	-2.05242400	-2.02135100
H	0.68958200	0.34293400	-1.87672800
H	0.28232000	-0.31895400	1.08331700
H	-1.12956200	1.54572000	-2.30567200
H	-2.73492900	1.19694100	-2.97734400
H	-2.57102200	1.78215800	-1.30261200
H	-1.46756500	-2.26184800	-2.26289700
H	-2.14518600	-1.20956500	-3.52652400
H	-0.48518200	-0.96301700	-2.96420900
H	5.97432800	-3.61417700	-0.65141600
H	6.72441600	-2.40468400	-1.71406400
H	7.62702000	-3.03991300	-0.34407300
H	6.02958600	-2.14510100	2.24240100
H	7.66281100	-2.07669400	1.54755500
H	6.79061800	-0.58385300	1.86968300

Table S13 Cartesian coordinate xyz of CDMA-DP probe molecule and MnO_4 in TS1 state.

	X	Y	Z
C	-2.73827100	-1.03976000	-1.19960500
C	-1.37622300	-0.97847600	-1.45106100
C	-0.50781800	-0.33497000	-0.56674500
C	-1.04447300	0.26960700	0.57610300
C	-2.40214800	0.22095800	0.83234600
C	-3.27092400	-0.43666300	-0.05366700
N	-4.65107200	-0.47972200	0.20574500
C	0.93442200	-0.28777200	-0.86913000
C	1.88520700	-0.39717200	0.18003600
C	-5.42120000	-1.60778100	-0.18282600
C	-5.30085500	0.62435200	0.81892900
C	-6.66841700	-1.43352000	-0.78702500
C	-7.42675300	-2.54068800	-1.15057500
C	-6.94602500	-3.82893100	-0.93074200
C	-5.69932500	-4.00141400	-0.33376600
C	-4.94231700	-2.90011100	0.04752400
C	-6.26505200	0.40868800	1.80645900
C	-6.91383300	1.48868800	2.39381900
C	-6.59951600	2.79183100	2.01607900
C	-5.63382500	3.00589800	1.03564900
C	-4.99237600	1.93088100	0.43155000
C	3.21286600	-0.71177500	0.01591300
C	3.93369500	-1.09003600	-1.26800800
O	5.31673800	-1.28710200	-0.83406200
C	5.42676200	-1.11436300	0.48120600
C	4.18191300	-0.76843000	1.04379500
C	6.68353100	-1.28802700	1.05662900
C	3.47673100	-2.43247300	-1.82785400
C	3.96394200	0.02255100	-2.30582700
C	3.90523400	-0.47013700	2.39449600
N	3.60633800	-0.21131800	3.47925100
C	6.90379100	-1.13664400	2.44527000
N	7.11010300	-1.02106000	3.57571300
C	7.78761000	-1.63324300	0.24032100
N	8.69214700	-1.91553700	-0.41994500
H	-3.39663200	-1.54289000	-1.89690700
H	-0.98207100	-1.43322800	-2.35362100
H	-0.39776100	0.79388000	1.27082900
H	-2.80266600	0.69265500	1.72118700
H	1.18901500	-0.73915200	-1.82102100
H	1.55636900	-0.17264900	1.18883700
H	-7.03918800	-0.43077300	-0.96557000
H	-8.39316600	-2.39311800	-1.61799600
H	-7.53676900	-4.68942000	-1.21989400
H	-5.31758000	-4.99874200	-0.14984000
H	-3.97785200	-3.03461900	0.52367400

H	-6.50344800	-0.60545700	2.10582500
H	-7.66027600	1.30932100	3.15856900
H	-7.10236800	3.63155800	2.47979700
H	-5.38579000	4.01467300	0.72730500
H	-4.25017700	2.09822600	-0.34051600
H	3.51109000	-3.19575100	-1.04894600
H	2.45927700	-2.37014900	-2.21216700
H	4.14004800	-2.72231900	-2.64419500
H	4.32463200	0.94947600	-1.85587400
H	4.63240200	-0.26693700	-3.11821000
H	2.96794800	0.19955600	-2.71097200
O	1.02071200	1.39422800	-1.56747100
Mn	1.66835400	2.75309200	-0.94899600
O	2.60883200	2.69506300	0.25331200
O	0.73307700	4.24283500	-1.15527300
O	1.83006500	4.14067900	-2.03606800

Table S14 Cartesian coordinate xyz of CDMA-DP probe molecule and MnO_4 in TS2 state.

	X	Y	Z
C	-2.58450500	0.73908400	1.37896300
C	-1.24865900	0.43458400	1.61535100
C	-0.55775200	-0.44216000	0.78376200
C	-1.23057100	-1.01171000	-0.29880100
C	-2.55870200	-0.70385600	-0.55118300
C	-3.25159800	0.17565700	0.28925700
N	-4.60846300	0.48915000	0.03647400
C	0.90059600	-0.75134200	1.02643300
C	1.77190800	-0.15522800	-0.01689000
C	-5.07008200	1.81733500	0.20790300
C	-5.50172700	-0.52366900	-0.38979000
C	-6.32328600	2.06313000	0.77732600
C	-6.77479800	3.36810200	0.93612100
C	-5.98112100	4.44424400	0.54668200
C	-4.72936600	4.19996000	-0.01300000
C	-4.27688600	2.89787400	-0.19050300
C	-6.46546300	-0.25190500	-1.36601700
C	-7.34432500	-1.24718700	-1.77668500
C	-7.26629400	-2.52820700	-1.23570700
C	-6.30128300	-2.80157300	-0.26952900
C	-5.42918400	-1.80778600	0.15925600
C	2.99373600	0.45073900	0.19829000
C	3.76208700	0.55147900	1.50419900
O	5.03496200	1.14767700	1.09672600
C	5.01654000	1.45776800	-0.19678000
C	3.79281400	1.06474100	-0.78496100
C	6.13837600	2.07635400	-0.73785000
C	3.13980400	1.54173300	2.48453800
C	4.08680600	-0.79713200	2.12921200
C	3.41602100	1.18799900	-2.13978400
N	3.04549500	1.25863100	-3.23055900
C	6.21170500	2.44325600	-2.10238500
N	6.29546100	2.75330500	-3.21136500
C	7.25290000	2.35769800	0.08993600
N	8.16405600	2.58995500	0.75990100
H	-3.11428200	1.41528600	2.03959400
H	-0.74459600	0.87962900	2.46711800
H	-0.70764300	-1.69925100	-0.95580000
H	-3.06911500	-1.14492100	-1.39936200
H	1.17461800	-0.40712200	2.02408800
H	1.34330900	-0.05049900	-1.00869000
H	-6.93933000	1.22841700	1.09098000

H	-7.74842800	3.54286800	1.37880700
H	-6.33350400	5.45995400	0.67759200
H	-4.10331900	5.02699300	-0.32692100
H	-3.30643000	2.71140000	-0.63559500
H	-6.52212900	0.74061500	-1.79756600
H	-8.08572100	-1.02118200	-2.53414100
H	-7.94836700	-3.30323700	-1.56290000
H	-6.23225000	-3.79197500	0.16499300
H	-4.68628500	-2.02205300	0.91878100
H	2.94993700	2.49473600	1.98822300
H	2.20164100	1.16160100	2.88660300
H	3.83249200	1.70073300	3.31244700
H	4.57212100	-1.44503000	1.39792300
H	4.75187300	-0.64798200	2.98125500
H	3.17452900	-1.28484800	2.47555300
O	1.05184100	-2.21247400	1.07213400
Mn	2.09796900	-3.17861900	0.07859900
O	2.79896500	-2.04147100	-0.72609300
O	1.88032100	-4.80413100	-0.60801200
O	2.89511900	-4.74158300	0.36858400

Table S15 Probe molecules excitation information.

Parameters / Probes	Oscillator Strength	Emission Wavelength (nm)	Sr (au)	Sm (au)	t(Å)	Excitation energy (eV)	Contributing Molecular Orbitals
CDMA-AM	1.86	543.57	0.72	0.43	-2.23	2.28	H→L 99.5%
CDMA-EA	1.88	543.38	0.72	0.44	-1.22	2.29	H→L 99.5%
CDMA-DM	1.92	568.03	0.69	0.41	-2.21	2.18	H→L 99.2%
CDMA-DP	1.12	717.35	0.53	0.24	1.64	1.73	H→L 98.7%

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