Electronic Supplementary Information

Conjugated Macro-Microporous Polymer Films Bearing Tetraphenylethylenes for the Enhanced Sensing of Nitrotoluenes

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Experimental Sections

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were obtained using a JSM6700F and a JEOL 2100F, respectively. Powder X-ray diffraction (PXRD) patterns were obtained using a Rigaku MAX-2200. The surface areas were obtained through the analysis of N_2 adsorption-desorption isotherm curves obtained at 77K using a Micromeritics ASAP2020. Pore size distribution was analyzed by the density functional theory (DFT) method. Thermogravimetric analysis (TGA) was conducted using under N_2 using a Seiko Exstar 7300. Infrared absorption spectra were obtained using a Bruker VERTEX 70 FT-IR spectrometer. UV/visible absorption spectra were obtained through diffuse reflectance spectroscopy using a SHIMADZU UN-3600. The emission spectra were obtained using a JASCO FP-6200. Solid state ^{13}C nuclear magnetic resonance spectroscopy (NMR) was conducted at CP-TOSS mode using a 500 MHz Bruker ADVANCE II NMR equipment at the NCIRF of Seoul National University. A 4 mm magic angle spinning probe was used with a spinning rate of 5 kHz.

Synthetic procedure for MA-CMP-F and control CMP-F

Silica spheres with an average diameter of 400 nm were prepared by the Stöber method.[1] In our work, the synthetic procedures were as follows. Ethanol (200 mL), water (23.5 mL), and ammonia solution (28-30%, 7 mL) were added to a 250 mL round bottomed flask. The solution was stirred at 600 rpm for 10 min. After tetraethylorthosilicate (TEOS, 17.5 mL, 74.2 mmol) was added to solution, the mixture was stirred with 600 rpm at room temperature for 18 h. The silica spheres were retrieved by centrifugation, washed with a 1:1 mixture of methanol and ethanol three times, and dried under vacuum. A slide glass plate (7.5 cm × 2.5 cm × 0.1 cm, Paul Marienfeld GmbH & Co.) was washed through sonication for 1 h in a mixture of 37% HCl (50 mL) and water (450 mL) in a 500 mL beaker. After the glass plate was washed with distilled water until the neuralization was confirmed, it was dried using N_2 flush. Silica spheres (0.30 g) were added to ethanol (60 mL) in a 70 mL vial and sonicated for 6 h. After the glass plate was added to the vial containing silica spheres, the

setting was added to oven at 50°C. After 4 days, the assembled silica spheres on the glass plate were obtained.

1,1,2,2-Tetra(4-bromophenyl)ethane and 1,1,2,2-tetra(4-ethynylphenyl)ethane were prepared by the synthetic procedures in the literature.[2] The glass plate with assembled silica spheres (the plate was cut to the size of 6 cm × 2.5 cm) was added to a Rodaviss glassware (100 mL). After $(PPh_3)_2PdCl_2$ (3.4 mg, 4.8 μmol), CuI (0.9 mg, 4.8 μmol), triethylamine (TEA, 30 mL), and toluene (20 mL) were added to the Rodaviss glassware, the mixture was stirred at 600 rpm for 1 h. The 1,1,2,2-tetra(4-bromophenyl)ethane (31 mg, 48 μmol) and 1,1,2,2-tetra(4-ethynylphenyl)ethane (21 mg, 48 μmol) were dissolved in toluene (3 mL). After the solution was added to the Rodaviss glassware, the mixture was stirred at 600 rpm for 10 min and heated at 80°C overnight *without stirring*. After being cooled to room temperature, the SiO_2@CMP/glass plate was taken out, washed with ethanol (100 mL) three times, and dried in an oven at 50°C for 3 h. For the etching of silica spheres, the SiO_2@CMP/glass plate was added to 10% HF aqueous solution (50 mL) in a square dish. The separated glass plate was removed after ~1 min. After the resultant MA-CMP-F was further treated with the HF solution for additional 2 h, it was washed with ethanol (100 mL) three times. The MA-CMP-F was transferred to polytetrafluoroethylene film (PTFE, thickness of 0.1 mm, Sigma Aldrich Co.) and dried in an oven at 80°C for 1 h.

For the preparation of control CMP-F, the same synthetic procedures as those of MA-CMP-F were applied except using TLC plate (Silica gel 60 F_{254} 25 aluminium sheets, Merck Milipore) with size of 6 cm × 2.5 cm instead of the glass plate with assembled silica spheres. In addition, ~ a half amount (24 ~ 28 μmol) of the 1,1,2,2-tetra(4-bromophenyl)ethane and 1,1,2,2-tetra(4-ethynylphenyl)ethane were used. Based on the experimental characterization of thickness of control CMP-F by SEM analysis, the CMP-F with a thickness of 2.3 μm was used for the sensing tests. The other synthetic procedures for CMP-F were the same as those for MA-CMP-F.

Synthetic procedure for MA-CMP-F bearing porphyrins in Figure 5[3]

Tetra(4-ethynylphenyl)porphyrin and tetra(4-ethynylphenyl) Cr-Cl porphyrin were prepared by the synthetic procedures in the literature.[4,5] The glass plate with assembled silica spheres (the plate was cut to the size of 6 cm × 2.5 cm) was added to a Rodaviss glassware (100 mL). After $(PPh_3)_2PdCl_2$ (1.3 mg, 1.9 μmol), CuI (0.3 mg, 1.6 μmol), and triethylamine (TEA, 10 mL) were added to a 10 mL vial, the solution was sonicated for 1 min and then, added to the Rodaviss glassware. After toluene (40 mL) was added to the Rodaviss glassware, the mixture was stirred for 2 h. Tetra(4-ethynylphenyl)porphyrin (25 mg, 35 μmol) and 1,4-diiodobenzene (23 mg, 70 μmol) were dissolved in THF (5 mL). After the solution was added to the Rodaviss glassware, the mixture was stirred at 600 rpm for 10 min and heated at 90°C overnight *without stirring*. After being cooled to room temperature, the SiO_2@CMP/glass plate was taken out, washed with ethanol (100 mL) three times, and dried in an oven at 50°C for 3 h. For the etching of silica spheres, the SiO_2@CMP/glass plate was added to 7.5% HF aqueous solution (50 mL) in a square dish. The separated glass plate was removed after ~1 min. After the

resultant MA-CMP-F was further treated with the HF solution for additional 2 h, it was washed with a mixture of methanol and water (100 mL) three times. The MA-CMP-F containing metal-free porphyrin was transferred to polytetrafluoroethylene film (PTFE, thickness of 0.1 mm, Sigma Aldrich Co.) and dried in an oven at 80°C for 1 h. For the preparation of MA-CMP-F containing Cr-F porphyrins, tetra(4-ethynylphenyl) Cr-Cl porphyrin (35 μmol) was used instead of tetra(4-ethynylphenyl) porphyrin. During the silica etching by HF, the Cr-Cl species in porphyrins were converted to Cr-F species, as reported in the literature.[5]

Experimental procedure of sensing tests

The sensing tests were conducted using MA-CMP-F or CMP-F with a size of 0.5 cm × 1 cm. The MA-CMP-F and CMP-F on the PTFE film were transferred to a slide glass plate and attached with a double side tape. DNT, 4NT, 2NT, 4CT, and T solution with concentrations of 0, 0.0025, 0.0050, 0.010, 0.15, 0.020, 0.050, 0.125, and 0.50 mM were prepared in ethanol. Each solution of 3 mL was used for the sensing tests. The emission intensity changes at 517 and 525 nm for MA-CMP-F and CMP-F, respectively, were measured using a JASCO FP-6200. Considering the conventional range of visible light, the excitation wavelength was fixed to 410 nm. After the MA-CMP-F and CMP-F on the glass plates were added to ethanol and left for 2 h until the system reached equilibrium with no changes of emission intensity, the solution was replaced with that with analytes. After leaving the system for 1 h, the changes of emission intensities were measured. K_{sv} values were measured by plotting I_o/I vs [M]; the Stern-Volmer plot ($I_o/I = K_{sv}[M] + 1$, I_o: the original emission intensity, I: the intensity of emission in the presence of analytes, M: the concentration of substrates in water, $R^2 > 0.99$ for linear regression) Recycling tests were conducted using 0 mM and 0.50 mM solutions of 4NT alternatively. Before each sensing cycle for 4 NT, the retrieved MA-CMP-F was washed with excess ethanol three times.

Procedure for computational simulation (Figures S3-5)

In order to shed light on the emission quenching behaviors of MA-CMP-F by nitrotoluenes, we performed the density functional theory (DFT) calculations on the HOMO-LUMO energy levels of MA-CMP-F and substrates. The geometrical optimizations for model systems of MA-CMP-F (CMP-1, CMP-4 and CMP-P refer to Fig. S5 in the ESI for the definition), TNT, DNT, 4NT, 2NT, 4-chlorotoluene (4CT), toluene (T), and additional toluene derivatives having monosubstituent at para position were carried out within B3LYP/light-tier1 level of theory using FHI-aims code.[6] The convergence criteria were set to 10^{-2} eV/Å except for the CMP-P case. For CMP-P, the PBE/light-tier1 level and 2×10^{-2} eV/Å of relaxation setting were used to conduct the periodic boundary condition (PBC) calculation with full relaxation for both atomic geometries and unit cell parameters, because computational costs for PBC calculations with hybrid functional are enormously expensive. Then, single point calculation at B3LYP/light-tier1 level was performed to estimate the HOMO and LUMO energy levels for CMP-P. It is noted that in a PBC calculation actually the HOMO and LUMO energy levels indicate the valence band maximum and conduction band minimum, respectively. The optimized unit

cell parameters of CMP-P were calculated to be 21.49 Å × 16.29 Å × 35.75 Å. The vacuum space of about 30 Å was added along the c-axis to avoid the interactions between 2-dimensional sheets. In addition, single point molar volume calculations at the optimized geometries for TNT, DNT, 4NP and 2NT were carried out to understand the size effect on the sensitivity of experimental sensing behavior using Gaussian 09 package.[7]

Theoretically, it is expected that the LUMO energy levels of MA-CMP-F are located around -2.31 ~ -2.89 eV which can possibly be modulated by the conjugation length of CMP moieties. The calculated relative LUMO energy levels of substrates indicate that the electron transfers from the excited MA-CMP-F to nitrotoluenes including TNT might be favorable to lead fluorescent quenching. On the other hand, the mismatch of LUMO energy levels 4CT and T prevents the induction of emission quenching of CMP materials, which is fully consistent with the experimental fluorescent sensing behavior. It is noteworthy that our DFT results indicate that MA-CMP-F can also be used for the detection of TNT compound. In the experimental results, the sensing efficiencies of MA-CMP-F towards nitrotoluenes were observed in the increasing order of DNT < 2NT < 4NT. This trend can be analyzed considering both the size and electronic effects of substrates. From the aspect of the diffusion process, we can speculate that smaller substrates (4NT and 2NT) would have higher sensing efficiencies than DNT. (Refer to Fig. S7 in the ESI for the calculated molar volume values and size parameters) In the case of 4NT and 2NT having similar molecular volumes, the calculated LUMO energy level of 4NT is rather lower than that of 2NT. Thus, the 4NT as photo-induced electron accepter has a better quenching efficiency than 2NT.

Reference

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Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Ciosolowski and D. J. Fox, *Gaussian 09, Revision B.01*, Gaussian, Inc., Wallingford CT, 2010.

Fig. S1 A photograph and SEM images of the 400 nm silica spheres assembled on the glass plate.

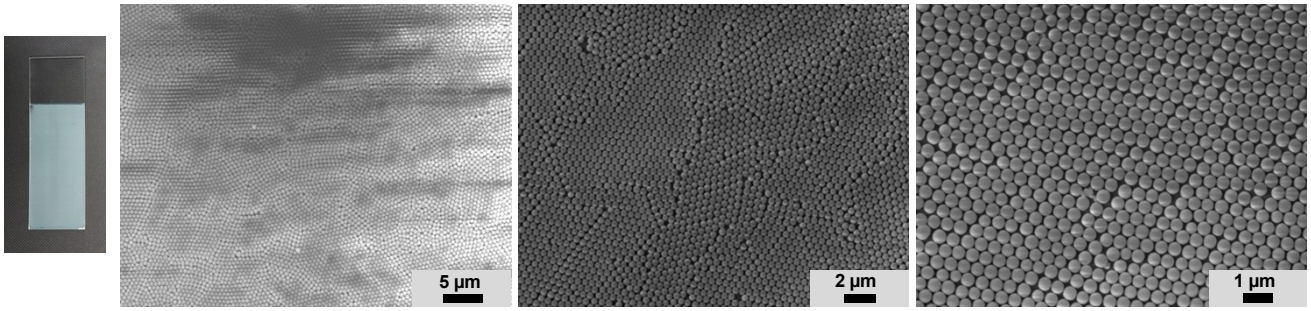


Fig. S2 Photographs and SEM images of 200 nm and 1.2 μm silica spheres assembled on the glass plate.

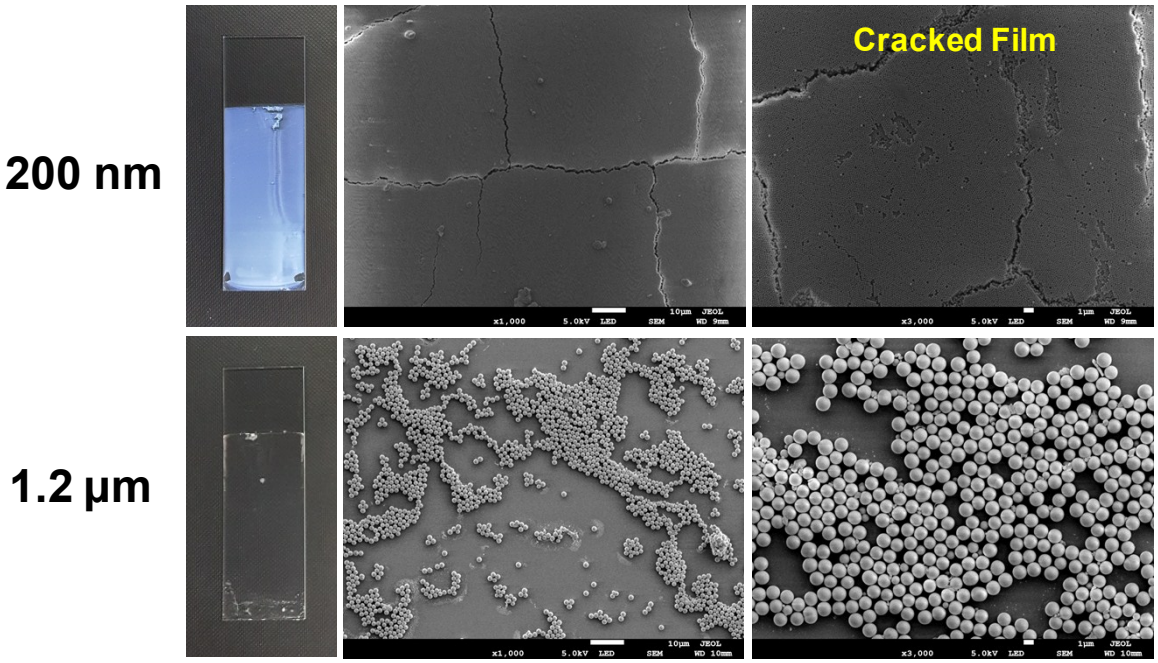


Fig. S3 Consideration of void space portion in MA-CMP-F induced by the 400 nm silica templates (supposing

the closest packing structure of hollow CMP spheres).

R = radius of silica spheres = 200 nm, a = edge distance of unit cell (nm)
$a = 2 \times 1.414 \times (R + 17.5)$ nm

Void space percent induced by silica templates
= {[Inter sphere void space + hollow space of 4 hollow spheres]/unit cell volume} × 100%
= {[unit cell volume – volume of 4 hollow CMP spheres + volume of 4 hollow space]/unit cell volume} × 100%
$= \{[a^3 - 4\times(4/3)\times\pi\ (R+17.5)^3 + 4\times(4/3)\times\pi\ R^3]/a^3\} \times 100\%$
$= \{[22.63(R+17.5)^3 - 16.76\ (R+17.5)^3 + 16.76\ R^3]/[22.63(R+17.5)^3]\} \times 100\%$
$= [0.2594 + 0.7406\ R^3/(R+17.5)^3] \times 100\ \% = 84\%$

Fig. S4 PXRD patterns of MA-CMP-F and CMP-F.

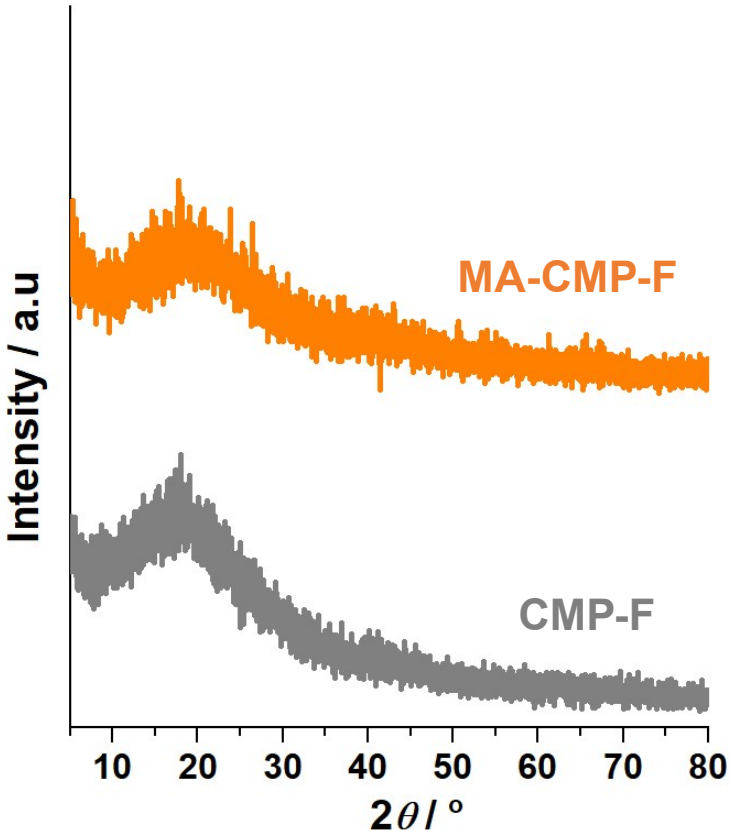


Fig. S5 Model systems (CMP-1, CMP-4, and CMP-P) of MA-CMP-F used for DFT simulation and their

optimized structures.

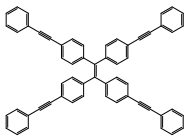
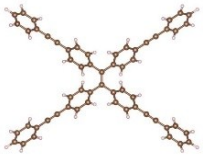
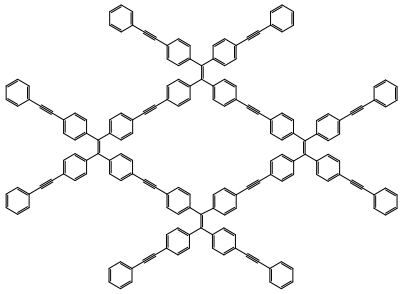
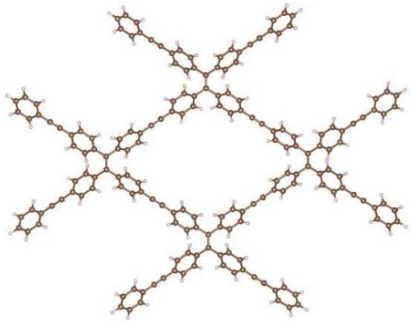
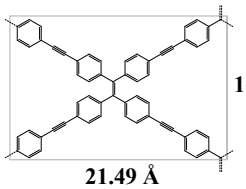
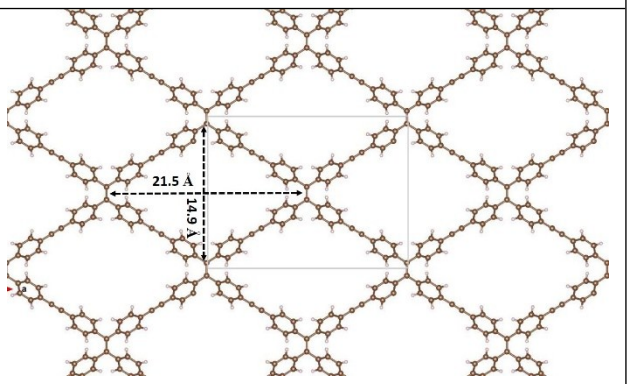
	Scheme	Optimized structures
CMP-1		
CMP-4		
CMP-P	**Unit cell**  **16.29 Å** **21.49 Å**	

Fig. S6 The cartesian coordinates (in Å) of optimized geometry for MA-CMP-F model systems.

CMP-1

C	0.00059224	0.68109457	-0.00044890
C	-0.00059158	-0.68095331	-0.00047384
C	-1.25071142	-1.48523383	-0.11427699
C	-1.48757635	-2.55271720	0.76334602
C	-2.19833166	-1.23618890	-1.11548089
C	-2.63994475	-3.31379140	0.67370933
H	-0.76156727	-2.78074184	1.53154976
C	-3.34625888	-2.00261315	-1.22308196
H	-2.03093296	-0.43228031	-1.81770592
C	-3.59510761	-3.05119574	-0.32247061
H	-2.81210849	-4.12115407	1.37103102
H	-4.06312160	-1.79617143	-2.00496046
C	1.24830764	-1.48689545	0.11367483
C	1.48414450	-2.55503417	-0.76347096
C	2.19583046	-1.23844872	1.11515332
C	2.63583289	-3.31710295	-0.67325817
H	0.75781004	-2.78307872	-1.53109019
C	3.34309298	-2.00573151	1.22323875
H	2.02887864	-0.43418440	1.81707763
C	3.59119117	-3.05476773	0.32303031
H	2.80728783	-4.12511556	-1.36995133
H	4.06008500	-1.79952211	2.00494992
C	1.25071388	1.48537869	-0.11421150
C	1.48757378	2.55282189	0.76348281
C	2.19834631	1.23637122	-1.11543288
C	2.63995805	3.31386810	0.67395044
H	0.76152368	2.78088590	1.53157411
C	3.34625551	2.00283537	-1.22305149
H	2.03098310	0.43245444	-1.81763488
C	3.59511869	3.05134112	-0.32229865
H	2.81204203	4.12130755	1.37111808
H	4.06316751	1.79633700	-2.00479335
C	-1.24830616	1.48703673	0.11369293
C	-1.48412115	2.55519524	-0.76345344
C	-2.19585390	1.23856544	1.11515657
C	-2.63581554	3.31724762	-0.67329024
H	-0.75773750	2.78332419	-1.53093660
C	-3.34309688	2.00588151	1.22328736
H	-2.02894366	0.43425497	1.81702786
C	-3.59118247	3.05492240	0.32303988
H	-2.80718607	4.12537464	-1.36979752
H	-4.06013643	1.79959677	2.00488994
C	-4.77434964	3.83407139	0.41687366
C	-5.78402337	4.49579368	0.48774057
C	-4.77846886	-3.83012635	-0.41638164
C	-5.78785896	-4.49232859	-0.48714149
C	4.77435579	-3.83391537	0.41684563
C	5.78401533	-4.49565669	0.48770833
C	4.77848272	3.83027796	-0.41620952
C	5.78788298	4.49246772	-0.48698349
C	6.97164981	-5.27274590	0.56341639
C	7.88706407	-5.08191919	1.61181573
C	7.25168402	-6.24539211	-0.41099830
C	9.04583660	-5.84175559	1.67846344
H	7.67744560	-4.33631755	2.36505663
C	8.41348552	-6.99960397	-0.33620667
H	6.55139117	-6.39769931	-1.21961648
C	9.31467554	-6.80164902	0.70656014
H	9.74139032	-5.68496194	2.49144766
H	8.61674313	-7.74423728	-1.09354996
H	10.21916838	-7.39143350	0.76153462
C	-6.97636960	-5.26809888	-0.56337802
C	-7.89106209	-5.07567384	-1.61203036
C	-7.25852574	-6.24025437	0.41089821
C	-9.05137762	-5.83315898	-1.67907776
H	-7.67956496	-4.33079607	-2.36556507
C	-8.42193437	-6.99200329	0.33592902
H	-6.55877117	-6.39401190	1.21976887
C	-9.32263567	-6.79208538	-0.70685863
H	-9.74647047	-5.67484820	-2.49200837
H	-8.62700808	-7.73604793	1.09341585
H	-10.22853023	-7.37973682	-0.76182185
C	-6.97169947	5.27282447	0.56341643
C	-7.25179084	6.24539366	-0.41106176
C	-7.88715604	5.08191639	1.61169550
C	-8.41368890	6.99945898	-0.33642002
H	-6.55149218	6.39770848	-1.21969028
C	-9.04597688	5.84169340	1.67835086
H	-7.67745098	4.33643348	2.36509635
C	-9.31487939	6.80150392	0.70638472
H	-8.61696854	7.74406393	-1.09374826
H	-9.74155069	5.68486364	2.49129522
H	-10.21944089	7.39118766	0.76128265
C	6.97642448	5.26819189	-0.56324180
C	7.25865267	6.24030516	0.41107350
C	7.89114568	5.07563775	-1.61176489
C	8.42213756	6.99193314	0.33618088
H	6.55889933	6.39411982	1.21992357
C	9.05148583	5.83309289	-1.67890180
H	7.67955254	4.33084420	-2.36543398
C	9.32280871	6.79199615	-0.70667911
H	8.62722974	7.73600197	1.09359305
H	9.74658394	5.67471392	-2.49179063
H	10.22875556	7.37956548	-0.76161948

CMP-4

C	12.09394936	11.07805813	25.53101775
C	12.81245447	9.52870822	23.83301632
C	13.25506407	11.81660618	25.35567601
H	11.36328475	11.39676589	26.26172071
C	13.97667776	10.26066067	23.65060650
H	12.64174869	8.64008177	23.24090003
C	14.21517292	11.41786533	24.41069245
H	13.43216586	12.70590701	25.94332540
H	14.71109093	9.94826385	22.92215477
C	15.40496624	12.17286288	24.22470187
C	16.41638216	12.81572042	24.06299300
C	17.60086710	13.57263801	23.86313911
C	17.85480815	14.72892391	24.61909459
C	18.55104605	13.18199777	22.90479131
C	19.00277123	15.47314981	24.40808200
H	17.14210563	15.03540532	25.37119057
C	19.70333302	13.92395745	22.71155082
H	18.37455992	12.29195346	22.31796278
C	19.94542182	15.09562228	23.44275179
H	19.17472366	16.36010761	25.00056364
H	20.42522677	13.59877279	21.97513726
C	21.19550909	15.87748561	23.22203785
C	31.77270982	8.87789067	23.15943686
C	31.77450326	7.51537211	23.16667393
C	30.54134039	6.70883133	22.94155171
C	30.22964817	5.63658159	23.78963417
C	29.68515148	6.96144629	21.86167664
C	29.09096397	4.87430831	23.59474285
H	30.88565646	5.40540241	24.61752146
C	28.55216742	6.19496371	21.65011580
H	29.91324853	7.76787083	21.17985198
C	28.22647408	5.14138322	22.52002676
H	28.85927681	4.06333024	24.27026684
H	27.90666502	6.40415028	20.80922238
C	33.00994282	6.71470227	23.40023181
C	33.32511914	5.63498024	22.56301191
C	33.86517816	6.98075256	24.47765304
C	34.46626470	4.87838607	22.76560740
H	32.67013305	5.39340877	21.73728931
C	35.00060581	6.22006433	24.69698778
H	33.63441833	7.79323059	25.15134656
C	35.32988707	5.15901845	23.83758694
H	34.70073980	4.06151976	22.09818584
H	35.64523928	6.43991062	25.53582631
C	33.02623080	9.68452755	23.14471333
C	33.18914991	10.75817086	24.03186136
C	34.05210234	9.43185028	22.22449785
C	34.34321792	11.52199442	24.03036651
H	32.40261227	10.98946351	24.73690097
C	35.20237275	10.20171020	22.20357055
H	33.94345397	8.62308748	21.51635413
C	35.37545472	11.25691659	23.11460417
H	34.45668083	12.33469653	24.73343502
H	35.97981219	9.99318343	21.48272175
C	30.51722797	9.68153357	23.16576012
C	30.35200672	10.74595441	22.26800664
C	29.49183757	9.43571418	24.08840823
C	29.19648717	11.50756882	22.26224606
H	31.13807774	10.97184931	21.56070517
H	28.34007393	10.20346448	24.10193690
H	29.60228116	8.63424845	24.80452160
C	28.16500123	11.24961278	23.18085876
H	29.08141840	12.31321680	21.55136740
H	27.56313549	10.00059056	24.82493628
C	26.98062264	12.03170076	23.18145642
C	25.97133293	12.69854126	23.17760492
C	27.05549637	4.36442323	22.31793016
C	26.05621925	3.70352089	22.15347638
C	36.50359853	4.38820770	24.04722397
C	37.50617843	3.73378061	24.21731146
C	36.55899623	12.04025906	23.10753529
C	37.56809915	12.70739782	23.10714844
C	38.68536508	2.96512283	24.41443317
C	39.57278251	3.27137987	25.45960756
C	38.98612217	1.88698186	23.56536638
C	40.72399260	2.52005574	25.64559162
H	39.34812817	4.09995197	26.11579828
C	40.13976443	1.14144768	23.75934957
H	38.30798994	1.64597227	22.75935073
H	41.39863304	2.76742531	26.45372346
H	40.35904631	0.31441668	23.09804488
C	24.87989655	2.92837996	21.96494307
C	23.98790985	3.22398810	20.92060504
C	24.58645110	1.85448610	22.82193103
C	22.83926292	2.46665316	20.74327371
H	24.20680428	4.04927824	20.25833975
C	23.43536605	1.10286854	22.63653491
H	25.26825332	1.62156866	23.62723847
H	22.16101437	2.70591634	19.93572195
H	23.22180118	0.27911289	23.30378877
C	24.78783035	13.48184231	23.17988849
C	24.54489473	14.42650167	22.16874273
C	23.82599083	13.32885525	24.19259150
C	23.39671064	15.19926821	22.18474084
H	25.26595568	14.54563846	21.37288549
C	22.67455905	14.09675805	24.19284769
H	23.99330878	12.60227877	24.97472026
C	22.44343226	15.06266701	23.20274374
H	23.23339450	15.92007850	21.39672072
H	21.94448805	13.95469282	24.97763153
C	38.75114486	13.49138568	23.10112322
H	38.99337363	14.43939049	24.10931970
C	39.71327311	13.33582499	22.08912033
C	40.14123014	15.21253525	24.09138317
H	38.27215248	14.56061267	24.90471057
C	40.86434438	14.10435470	22.08680872
H	39.54717902	12.60567181	21.31006446
C	41.09497053	15.07323790	23.07417692
H	40.30425558	15.93547207	24.87750852
H	41.59509393	13.95882939	21.30329798
C	42.34332227	15.88732351	23.05471636
C	51.43843132	11.08134456	20.73700506
C	50.71285458	9.52138545	22.42211041
C	50.27924843	11.82208505	20.91617890
H	52.17127359	11.40349833	20.00999820
C	49.55057274	10.25545513	22.60835222
H	50.87999923	8.62784202	23.00781712
C	49.31655750	11.41908290	21.85664335
H	50.10668453	12.71659082	20.33513394
H	48.81422547	9.93967697	23.33338825
C	48.12867318	12.17612383	22.04634509
C	47.11921227	12.82131165	22.21094968
C	45.93618011	13.57984280	22.41293831
C	45.68407431	14.73799091	21.65928082
C	44.98518306	13.18871934	23.37021504
C	44.53695817	15.48318020	21.87126739
H	46.39732655	15.04502094	20.90794496
C	43.83368506	13.93171415	23.56446022
H	45.15970493	12.29656208	23.95441988
C	43.59318120	15.10493551	22.83527798
H	44.36626429	16.37139286	21.28030953
H	43.11074076	13.60419585	24.29883112
C	12.08862927	22.03831943	20.78170938
C	12.81807015	23.58808800	22.47457215
C	13.24956098	21.29818684	20.95173779
H	11.35365021	21.71998259	20.05517143
C	13.98213769	22.85458902	22.65166217
H	12.65155452	24.47734186	23.06695284
C	14.21509021	21.69633097	21.89141378
H	13.42190972	20.40798703	20.36403445
H	14.72052434	23.16672034	23.37620249
C	15.40462353	20.93966468	22.07223953
C	16.41543787	20.29483038	22.22981253
C	17.60000006	19.53687629	22.42511026
H	18.55425986	19.92716662	23.37949243
C	17.85048459	18.38044008	21.66831024
H	19.70693936	19.18466844	23.56844924
H	18.38119366	20.81821124	23.96582499
C	18.99882729	17.63558004	21.87514890
H	17.13493269	18.07432148	20.91878010
C	19.94546831	18.01261625	22.83681345
H	20.43226026	19.51162874	24.30073800
H	19.16796317	16.74846423	21.28208839
C	21.19576811	17.22988272	23.05302400
C	31.76542526	25.60217438	23.10737462
C	31.76672742	24.23966285	23.11056669
C	30.51329852	23.43282357	23.10134154
C	30.35070733	22.36553829	23.99622452
C	29.48729494	23.67855670	22.17936865
C	29.19691544	21.60133119	24.00025515
H	31.13745054	22.13957905	24.70275272
C	28.33723771	22.90823253	22.16409373
H	29.59576506	24.48212933	21.46531720
C	28.16451216	21.85954453	23.08272628
H	29.08373381	20.79363394	24.70910936
H	27.55968619	23.11127253	21.44180154
C	33.02220581	23.43597663	23.12453613
C	33.18926968	22.36598080	22.23380732
C	34.04566650	23.68762849	24.04769163
C	34.34493955	21.60454263	22.23500552
H	32.40472763	22.13557606	21.52625220
C	35.19751277	22.92014199	24.06825805
H	33.93377568	24.49360279	24.75850263
C	35.37461056	21.86841559	23.15398246
H	34.46160361	20.79459323	21.52928969
H	35.97297652	23.12780597	24.79147985
C	32.99974717	26.40619282	22.87921627
C	33.31114630	27.48300281	23.72160141
C	33.85799014	26.14595580	21.80280817
C	34.45182463	28.24189244	23.52521762
H	32.65358050	27.72021102	24.54654387
C	34.99300725	26.90906751	21.58964215
H	33.63012708	25.33596988	21.12513009
C	35.31879161	27.96673457	22.45449756
H	34.68346845	29.05626216	24.19667003
H	35.64007651	26.69347322	20.75158557
C	30.53021438	26.40552599	23.33281790
C	30.21798892	27.47979635	22.48750634
C	29.67261410	26.14803941	24.41042126
C	29.07761702	28.23946340	22.68284049
H	30.87487266	27.71471655	21.66136494
C	28.53792699	26.91188675	24.62245671
H	29.90081238	25.33980111	25.09005932
C	28.21183267	27.96761132	23.75531727
H	28.84555230	29.05207349	22.00940242
H	27.89147858	26.69876436	25.46163226
C	27.03922381	28.74192689	23.95808254
C	26.03791682	29.39964076	24.12289777
C	26.98122707	21.07574862	23.08154979
C	25.97190404	20.40894750	23.08673206
C	36.55950555	21.08715008	23.16142398
C	37.56874610	20.42022938	23.16273700
C	36.49258891	28.73938975	22.25208222
C	37.49453464	29.39626129	22.08769916
C	38.75203043	19.63665722	23.17006282
C	39.71250307	19.79214519	24.18364369
C	38.99590719	18.68874245	22.16218415
C	40.86357372	19.02361061	24.18785181
H	39.54451416	20.52126718	24.96326200
C	40.14357728	17.91539157	22.18217755
H	38.27604078	18.56765359	21.36554376
C	41.09567266	18.05462836	23.20095415
H	41.59286105	19.16902361	24.97274748
H	40.30776861	17.19225799	21.39648066
C	24.78875246	19.62506009	23.08606200
C	23.82443754	19.77805724	22.07574272
C	24.54835428	18.68003979	24.09747812
C	22.67308029	19.00997264	22.07809104
H	23.98927553	20.50563161	21.29401258
C	23.40021053	17.90712666	24.08410652
H	25.27135004	18.56066864	24.89154297
C	22.44430737	18.04390433	23.06859350
H	21.94083328	19.15364730	21.29563132
H	23.23885274	17.18621260	24.87243952
C	24.86004757	30.17206376	24.31306955
C	24.56515263	31.24846472	23.45976776
C	23.96773852	29.87076388	25.35553735
C	23.41229297	31.99696343	23.64692856
H	25.24711489	31.48578414	22.65588913
C	22.81736629	30.62502312	25.53468276
H	24.18789840	29.04355945	26.01498055
H	23.19751164	32.82261246	22.98241891
H	22.13892981	30.38153084	26.34081148
C	38.67431279	30.16647588	21.90033965
C	38.97150797	31.23887324	22.75793681
C	39.56609871	29.86730787	20.85685770
C	40.12600001	31.98562148	22.57398682
H	38.29005918	31.47431283	23.56280188
C	40.71812186	30.61979217	20.68093987
H	39.34438914	29.04305070	20.19425603
H	40.34252061	32.80806068	23.24189870
H	41.39629365	30.37784711	19.87411433
C	42.34360223	17.23997193	23.22264996
C	51.43733510	22.03966081	25.55824526

C	50.71569330	23.60091301	23.87260647
C	50.27785344	21.29992503	25.37689105
H	52.16873933	21.71663551	26.28631534
C	49.55312927	22.86786722	23.68421291
H	50.88453703	24.49452766	23.28747942
C	49.31698582	21.70409556	24.43503356
H	50.10339614	20.40531723	25.95725290
H	48.81814645	23.18451072	22.95816718
C	48.12872263	20.94824333	24.24287652
C	47.11870038	20.30450780	24.07603089
C	45.93584845	19.54643881	23.87103709
C	44.98677660	19.93787078	22.91199478
C	45.68228529	18.38803579	24.62392559
C	43.83552892	19.19504900	22.71564108
H	45.16270597	20.82981670	22.32789517
C	44.53548070	17.64304058	24.40982334
H	46.39404247	18.08111994	25.37673227
C	43.59346137	18.02176236	23.44431432
H	43.11400862	19.52181989	21.97956142
H	44.36360010	16.75469841	25.00022622
C	22.53443059	31.68948206	24.68297952
H	21.63662762	32.27484351	24.82539398
C	11.86747013	23.18438818	21.54077951
C	41.00325814	31.68033194	21.53681382
C	11.86726416	9.93299265	24.77203087
C	41.01264971	1.45370727	24.79815006
H	41.91110186	0.87068668	24.94596659
C	22.55780378	1.40468964	21.59856281
C	51.66059570	9.92984758	21.48748983
H	52.56541486	9.35535818	21.34520943
C	51.66162849	23.19128175	24.80856181
H	52.56668793	23.76498797	24.95249303
H	41.90256543	32.26392672	21.39645813
H	10.96119574	23.75836244	21.40575515
H	10.96093971	9.36006828	24.91111180
H	21.66136683	0.81694860	21.45737502

CMP-P

C	10.63075739	8.70591649	19.58547846
C	10.62646535	7.33218841	19.58449560
C	9.37298037	6.53257770	19.52672885
C	9.18734058	5.47124813	20.43600276
C	8.35517687	6.78733431	18.58716284
C	8.01033472	4.73345199	20.45069384
C	7.18056724	6.04404104	18.58277872
C	6.97604475	5.01423826	19.52930880
C	11.87596792	6.52627842	19.64151282
C	12.06073785	5.47034557	18.72559742
C	12.89060212	6.77073994	20.58695745
C	13.23540810	4.72908816	18.70952155
C	14.06276279	6.02348210	20.59032846
C	14.26746095	5.00051274	19.63644675
C	11.88445746	9.50497164	19.52589878
C	12.07545304	10.56099897	20.44046187
C	12.89700757	9.25457253	18.57976609
C	13.25360260	11.29672069	20.45442745
C	14.07208745	9.99707622	18.57349108
C	14.28263307	11.02048122	19.52549946
C	9.38198596	9.51290226	19.64595002
C	9.19661861	10.56918763	18.73066729
C	8.36926871	9.26979107	20.59387949
C	8.02303607	11.31219767	18.71745487
C	7.19829476	10.01892325	20.60018626
C	6.99284935	11.04236880	19.64684879
C	5.78490362	11.78026679	19.61539652
C	4.74056990	12.41600829	19.56871390
C	5.76579086	4.28011334	19.56136664
C	4.72043563	3.64618728	19.60998839
C	15.47620306	4.26403539	19.60226822
C	16.52059215	3.62898557	19.54816146
C	15.49414380	11.75263704	19.55529381
C	16.53997768	12.38557780	19.60636791
C	17.72811456	2.89079223	19.51014950
C	18.76261300	3.15513873	20.43593310
C	17.92692320	1.86851652	18.55426068
C	19.93439651	2.40926556	20.41495182
C	19.09568950	1.11593503	18.55321052
C	20.11411097	1.35500229	19.49607958
C	3.51185063	2.90918003	19.63847171
C	2.47982687	3.18437611	18.71289386
C	3.30902052	1.87865214	20.58483490
C	1.30714297	2.43968713	18.72330065
C	2.13909797	1.12802209	20.57562381
C	1.12417012	1.37696927	19.63148886
C	3.53233182	13.15357550	19.54110960
C	3.33067129	14.18996925	18.60083487
C	2.49901398	12.87175358	20.46306755
C	2.15993010	14.93911036	18.61227645
C	1.32574812	13.61529315	20.45517266
C	1.14346168	14.68348337	19.55307967
C	17.74802565	13.12312550	19.64186836
C	17.95236631	14.14124920	20.60122174
C	18.77764034	12.86137741	18.70966879
C	19.12137651	14.89334418	20.59844568
C	19.94930560	13.60742514	18.72622621
C	20.13369542	14.65826746	19.64797582
C	21.38348345	15.46402686	19.59428849
C	21.36462671	0.55016831	19.54587578
H	9.97582260	5.24021398	21.15456864
H	8.48845393	7.58614323	17.85689613
H	7.87017360	3.93409747	21.17910348
H	6.40031398	6.25677835	17.85160532
H	11.27319248	5.24690858	18.00354636
H	12.75771401	7.56527714	21.32231389
H	13.37500343	3.93236850	17.97809512
H	14.84143597	6.22725695	21.32604707
H	11.29027787	10.78911042	21.16360553
H	12.76050114	8.45716108	17.84851571
H	13.39833960	12.09248680	21.18586713
H	14.84944372	9.78926696	17.83779134
H	9.98259754	10.79141772	18.00655907
H	8.50306005	8.47510779	21.32895883
H	7.88272344	12.10900595	17.98627140
H	6.42130645	9.81633601	21.33802973
H	18.62770927	3.94834109	21.17201655
H	17.14490253	1.66929167	17.82114208
H	20.72371580	2.62869107	21.13624243
H	19.22062082	0.32015326	17.81816373
H	2.61707411	3.98637383	17.98680522
H	4.08768169	1.67190378	21.31973669
H	0.51960520	2.66696512	18.00244281
H	2.00760975	0.32823309	21.30555630
H	4.11217223	14.40265722	17.87090568
H	2.63575154	12.06498793	21.18390525
H	2.03010078	15.74489247	17.88903815
H	0.53655607	13.38393509	21.17286664
H	17.17522436	14.33675815	21.34078771
H	18.63931797	12.06874680	17.97356402
H	19.25431597	15.68333010	21.33871159
H	20.73506814	13.39082153	18.00016368

Fig. S7 The calculated molar volumes (in cm^3/mol) and size parameters of nitrotoluene substrates (TNT, DNT,

4NP and 2NT) at B3LYP/6-31+G(d,p) level of theory with Gaussian 09 packages.

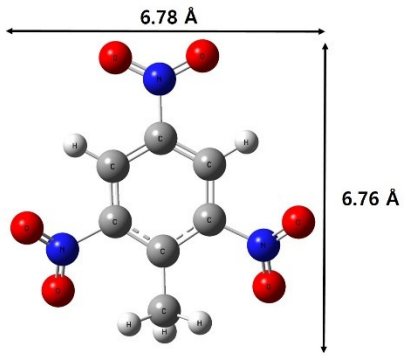
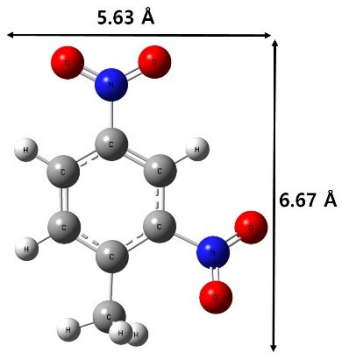
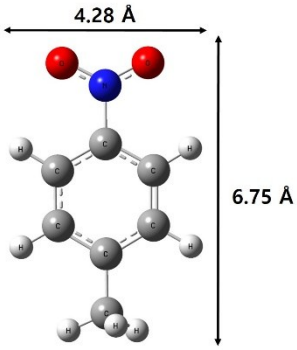
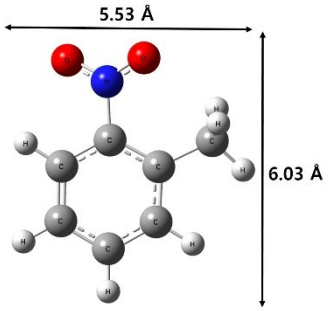
 Molar volume: 137.9 cm^3/mol **TNT**	 Molar volume: 124.3 cm^3/mol **DNT**
 Molar volume: 101.1 cm^3/mol **4NT**	 Molar volume: 98.5 cm^3/mol **2NT**

Fig. S8 The Stern-Volmer plots (I_o/I vs [M]) of the emission quenching of MA-CMP-F and CMP-F by 4NT,

2NT, and DNT.

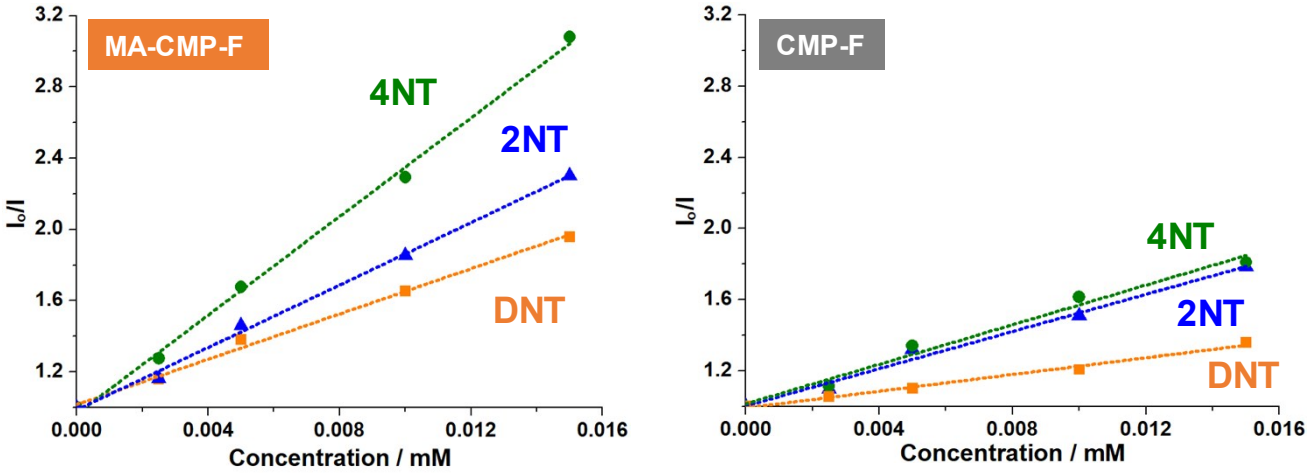


Fig. S9 Low magnification SEM image of MA-CMP-F recovered after the fifth recycle tests.

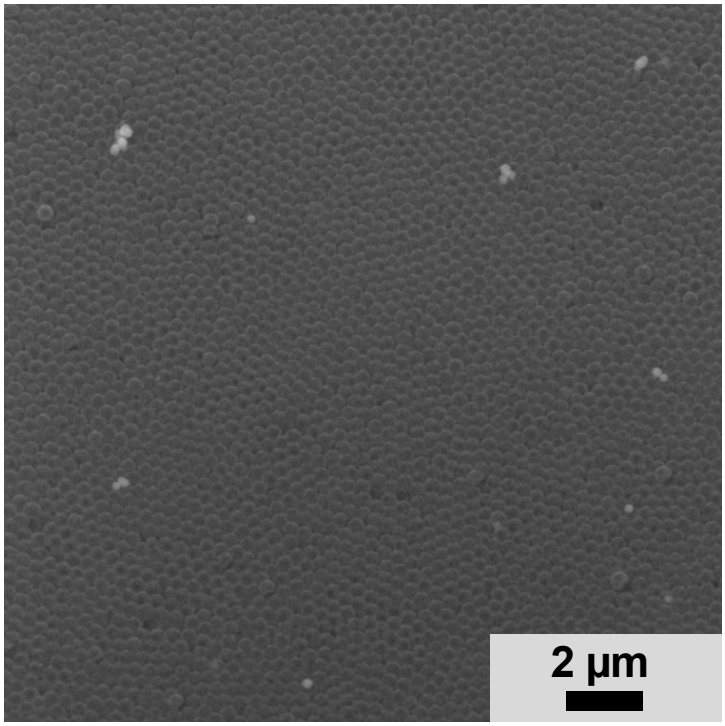


Fig. S10 Photographs of emission quenching of MA-CMP-F by 4NT.

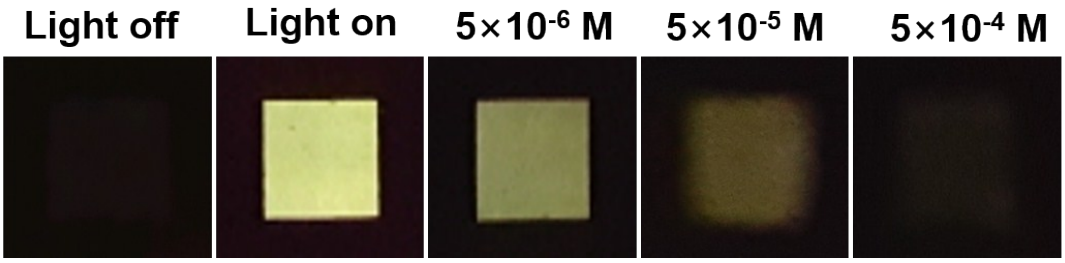
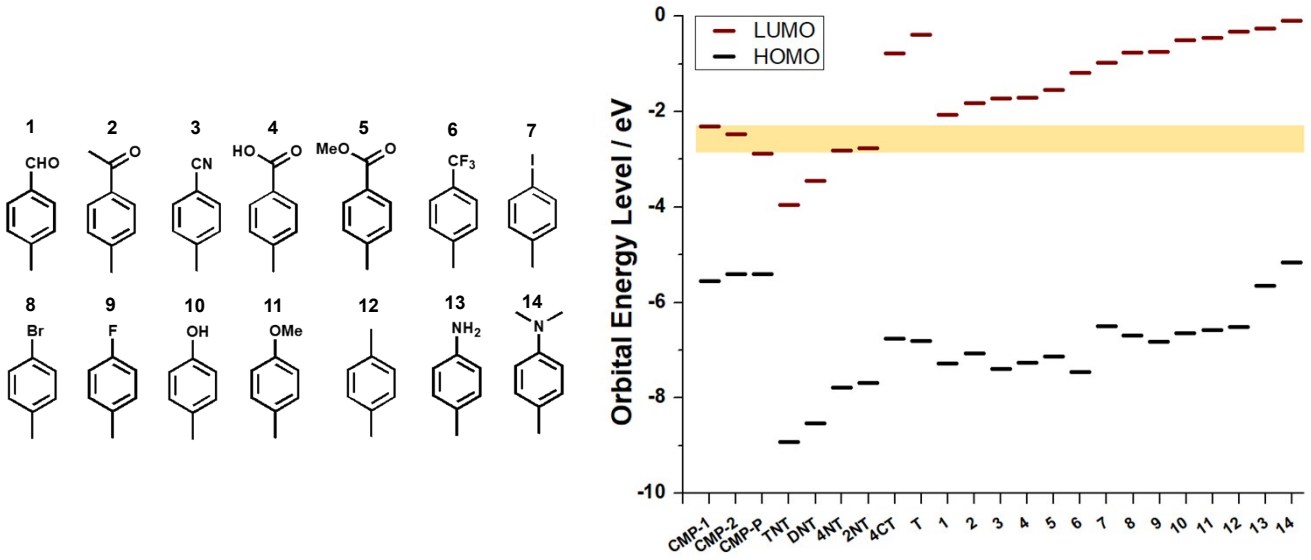


Fig. S11 The simulated HOMO and LUMO energy levels of additional toluene derivatives.



Entry	Systems	LUMO level (eV)	HOMO level (eV)	Entry	Systems	LUMO level (eV)	HOMO level (eV)
1	**CMP-1**	-2.31	-5.55	13	**4**	-1.71	-7.26
2	**CMP-2**	-2.47	-5.40	14	**5**	-1.54	-7.13
3	**CMP-P**	-2.89	-5.40	15	**6**	-1.18	-7.45
4	**TNT**	-3.96	-8.92	16	**7**	-0.98	-6.50
5	**DNT**	-3.44	-8.53	17	**8**	-0.77	-6.69
6	**4NT**	-2.82	-7.78	18	**9**	-0.74	-6.82
7	**2NT**	-2.77	-7.68	19	**10**	-0.50	-6.64
8	**4CT**	-0.78	-6.76	20	**11**	-0.46	-6.58
9	**T**	-0.39	-6.80	21	**12**	-0.32	-6.51
10	**1**	-2.07	-7.27	22	**13**	-0.26	-5.65
11	**2**	-1.82	-7.07	23	**14**	-0.09	-5.17
12	**3**	-1.72	-7.38				

Fig. S12 (a-c) The emission quenching behavior of MA-CMP-F in ethanol by O_2 and NO_2 in nitrogen (the

gases were bubbled into ethanol solution before measurements.) (d-e) The influence of O2 and NO2 in the emission quenching of MA-CMP-F in ethanol by 4NT (0.015 mM).

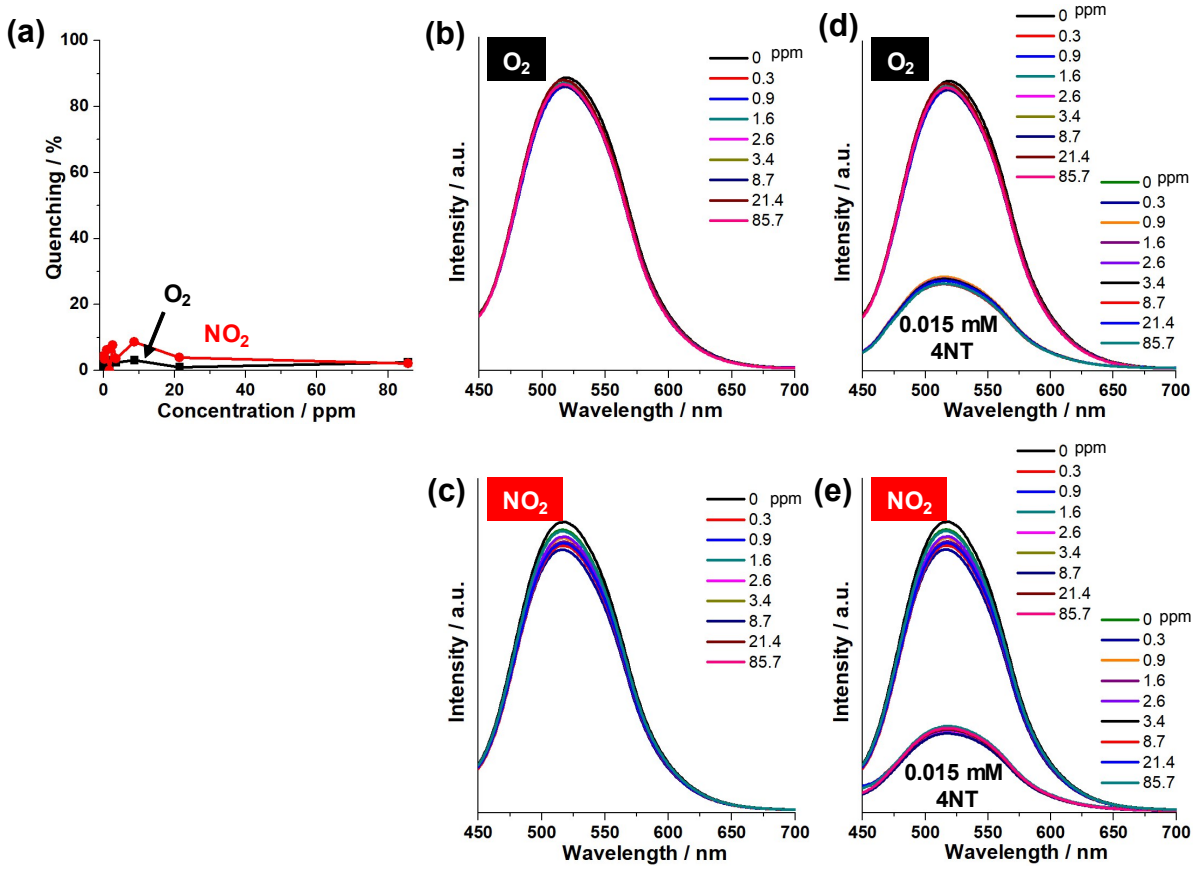


Fig. S13 (a) The emission quenching behavior of MA-CMP-F in ethanol by tetrabutylammonium perchlorate

and nitrate and (b) the Stern-Volmer plots.

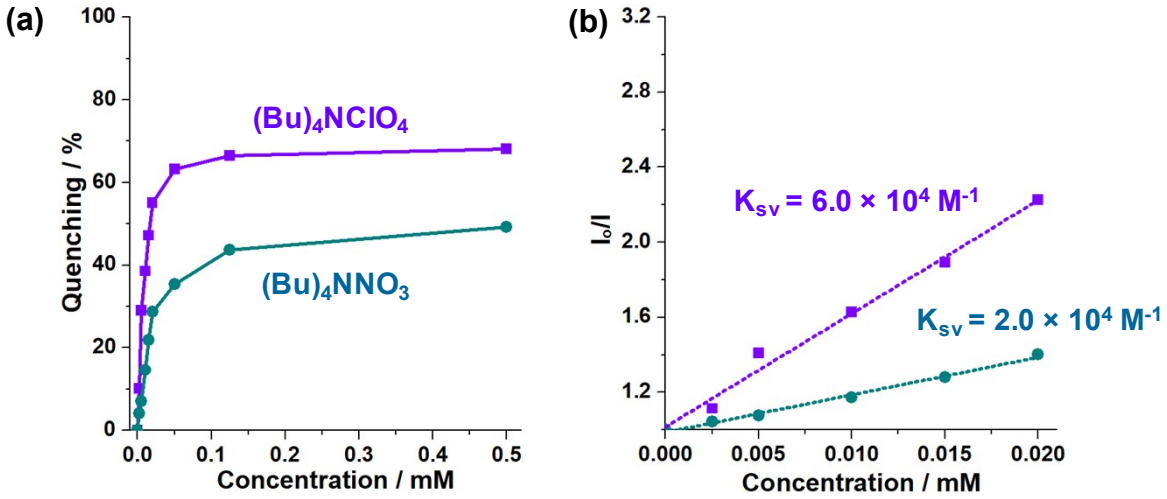


Fig. S14 (a) UV/vis absorption and (b) IR spectra of MA-CMP-F containing metal-free porphyrin and Cr-F

porphyrin moieties. In UV/vis absorption spectra, the Q band peak of MA-CMP-F with metal-free porphyrins appeared at 655 nm (indicated by asterisk), confirming the metal-free porphyrin species. In IR spectra, the vibration peak of MA-CMP-F with Cr-F porphyrins appeared at 1010 cm^{-1}, indicating the Cr-porphyrin species. For the synthetic details, refer to experimental procedures in the ESI.

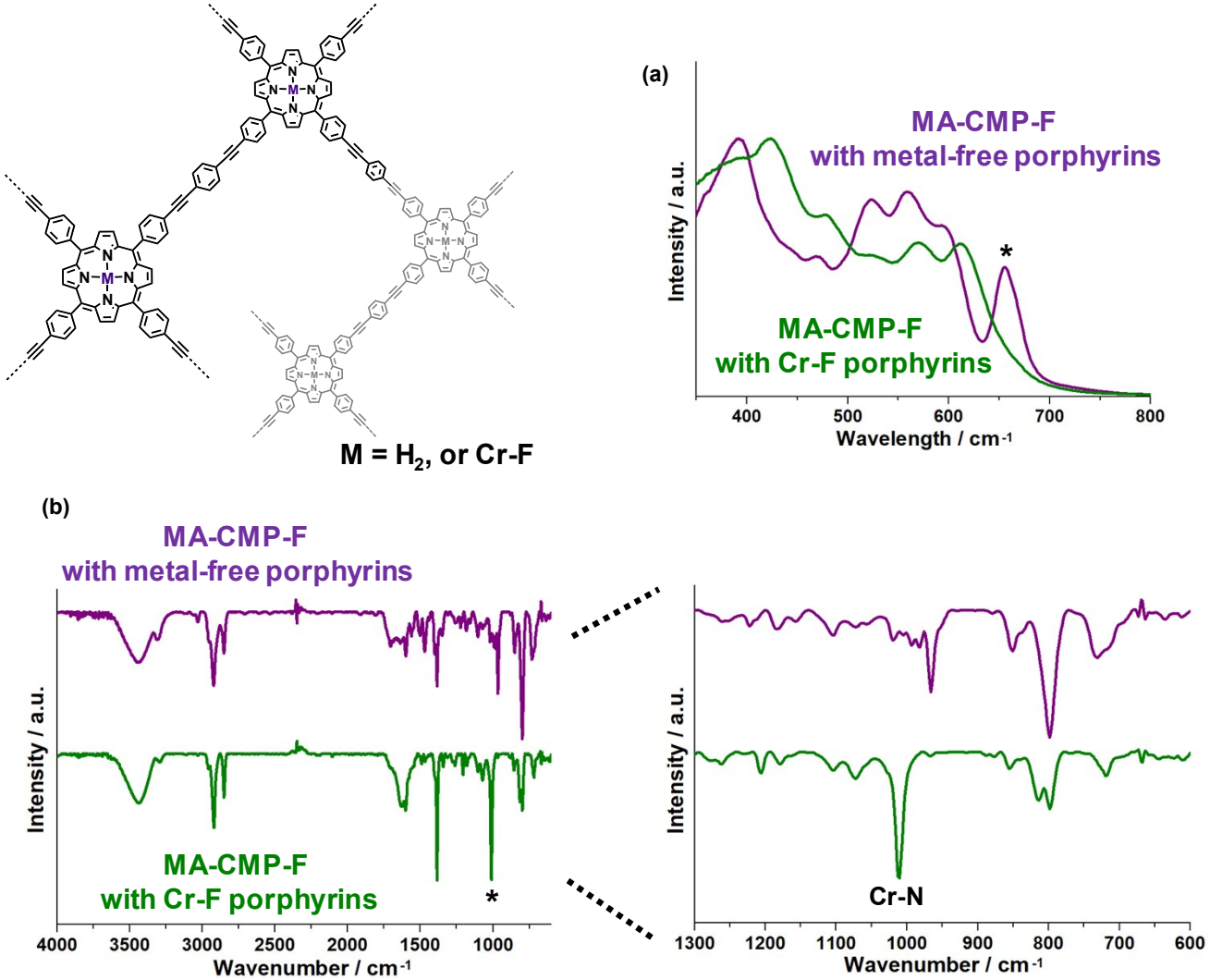


Table S1 Comparison of the sensing performance of MA-CMP-F with the results (best K_{sv} value) of emissive

CMP materials in the literature. TNP=2,4,6-trinitrophenol, TNB=1,3,6-trinitrobenzene, DNT=2,4-dinitrotoluene, TNT=2,4,6-trinitrotoluene, 2NP=2-nitrophenol, 4NT=4-nitrotoluene.

Entry	Materials	Substrate	Solvent	ex	K_{sv} (M^{-1})	ref
1	Microporous organic polymer with Troger base and TPEs	TNP	ethanol	380	**26000**	17
2	Nanoporous polymers with silsesquioxane and TPEs	-	chloroform	350	**-**	18
2	Dynamic covalent imine get	TNP	water	469	**32220**	19
3	Microporous polymer films with carbazole, thiophene, TPE	TNB	acetonitrile	340	**67800**	20
4	Nanofibrous PTBPE/PLA films	TNB	vapor	394, 380	**-**	21
5	Porous polymer films with carbazole and TPE	TNP	acetonitrile	331	**64000**	22
6	Porous polymer films with carbazole and TPE	DNT	acetonitrile	331	**790**	22
7	Conjugated porous polymer film	TNT	vapor	396	**-**	23
8	Conjugated microporous polymers with carbarzole derivatives	DNT	acetonitrile	368	**5900**	31
9	Covlent organic polymer	TNP	THF	365	**14500**	32
10	Microporous organic polymers containing ethenylphenyl unit	TNP	THF: H_2O=9:1	365	**-**	33
11	Carbazole based conjugated microporous polymer	4NT	THF	380	**4300**	34
12	Porous hyperbranched conjugated polymer with triphenylamine	TNT	THF	353	**1380**	35
13	Sn-porphyrin network film	TNP	water	422	**24000**	36
14	Covalent organic polymer	TNT	methanol	365	**2271**	37
15	Highly cross-linked polymer with curcumins	TNP	methanol	372	**15200**	38
16	Hollow microporous organic network	TNP	THF:H_2O=1:2	440	**15000**	39
17	Conjugated porous polymer with carbazole and triphenylamine	2NP	dioxane	510	**61200**	40
18	Conjugated microporous polymers with fluorescein	TNP	THF	500	**2080**	41
19	MA-CMP-F	4NT	ethanol	410	**138600**	This work