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Polarization engineering of porous organic polymer for superior photocatalytic synthesis of disulfide and CO_2 reduction

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Computational methods

The first-principles calculations based on the Density Functional Theory (DFT) were performed using the Materials Studio software with CASTEP and DMol3 model. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional within the generalized gradient approximation (GGA) was employed to describe the exchange-correlation energy. The energy cutoff for the plane wave basis expansion was set to 600 eV. The force on each atom was set as 0.03 eV/Å for convergence criterion. Slab model was constructed in a 4×4 supercell, with a vacuum layer of 20 Å in the z direction to avoid the interaction between layers. The sampling in the Brillouin zone was set with 3×3×1 by the Monkhorst-Pack method. The van der Waals interaction was considered by using DFT-D3 method.

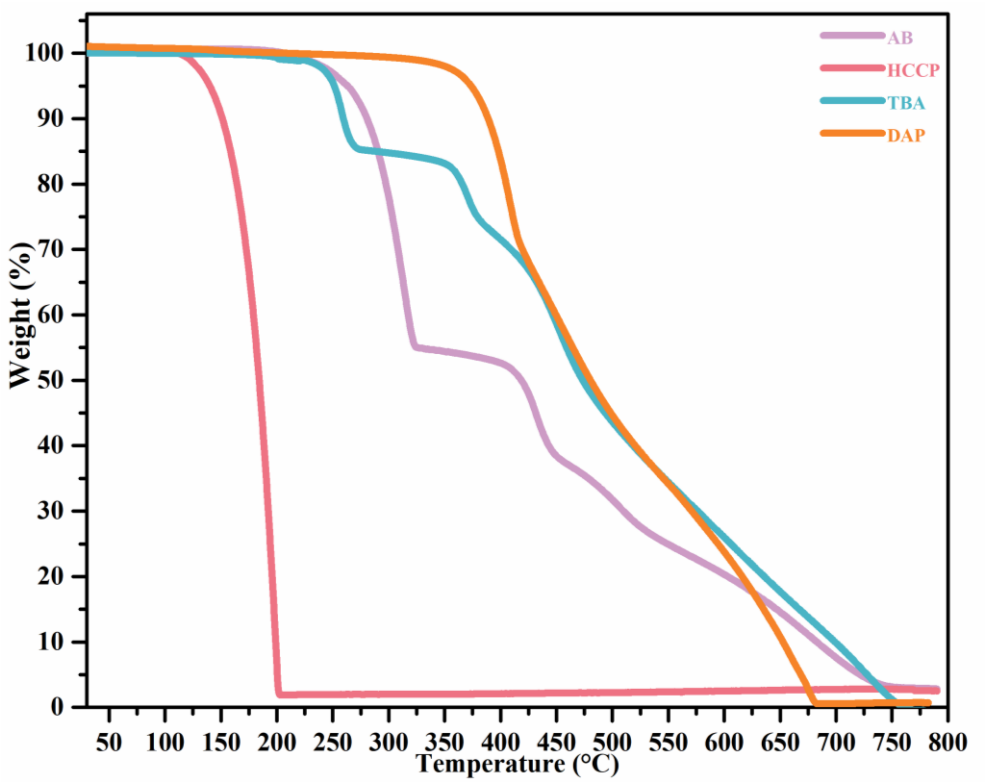

Fig. S1. Thermogravimetric analysis results of AB (barbituric acid), HCCP (hexachlorocyclotriphosphazene), TBA (2-thiobarbituric acid), and DAP (2-Amino-4,6-dihydroxypyrimidine).

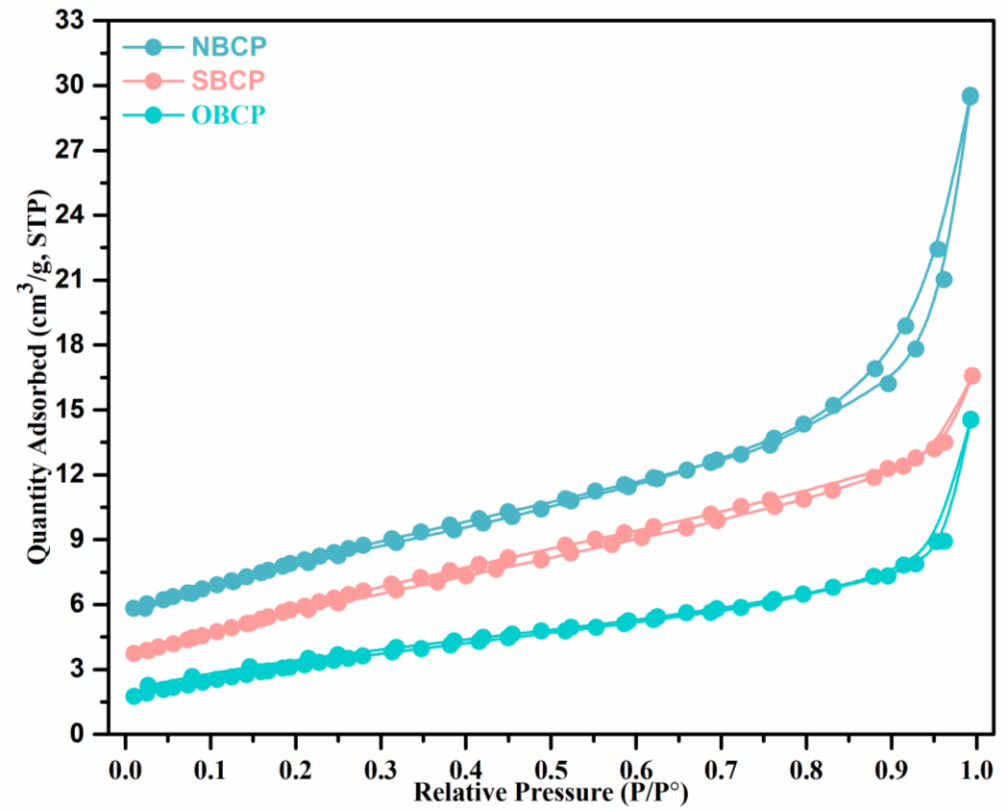

Fig. S2. N_2 adsorption-desorption isotherm of NBCP, SBCP and OBCP.

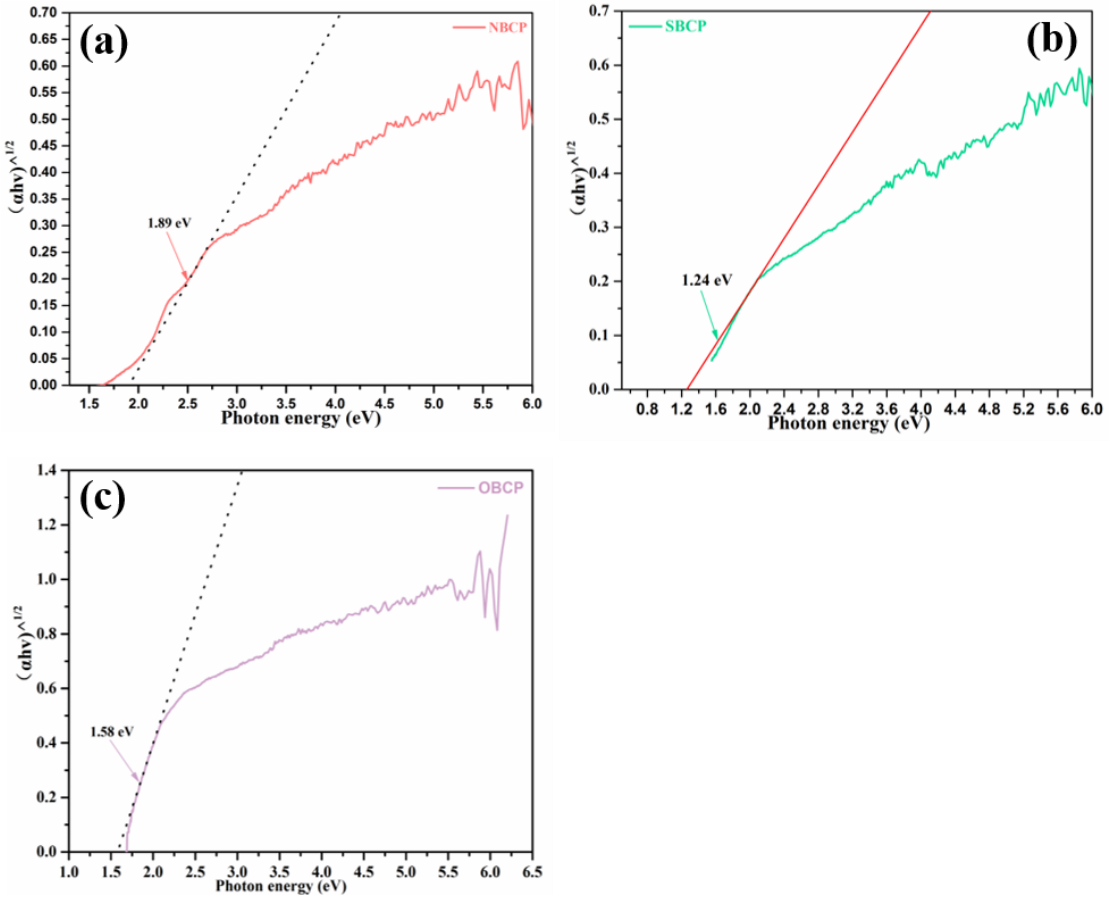

Fig. S3. UV–vis diffuse reflectance spectra measured from samples as indicated by the legends. Plot of $(ahv)^{1/2}$ vs hv.

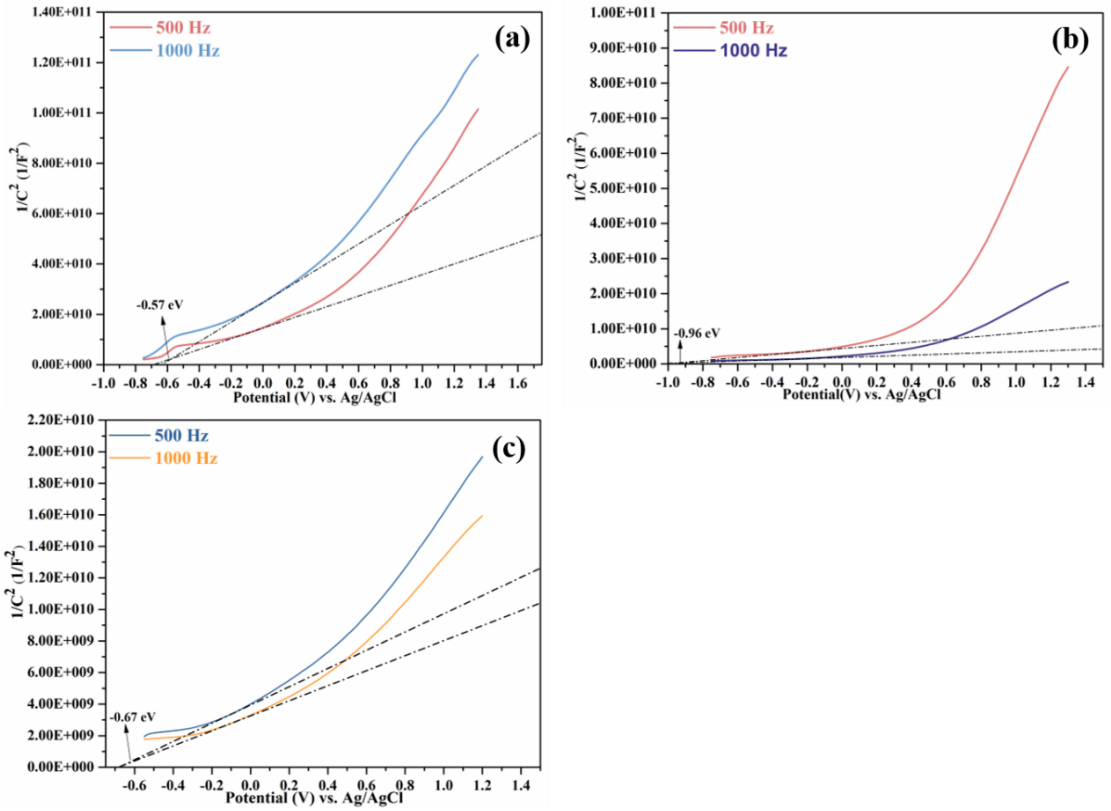

Fig. S4. Mott-Schottky plots of (a) NBCP, (b) OBCP and (c) SBCP.

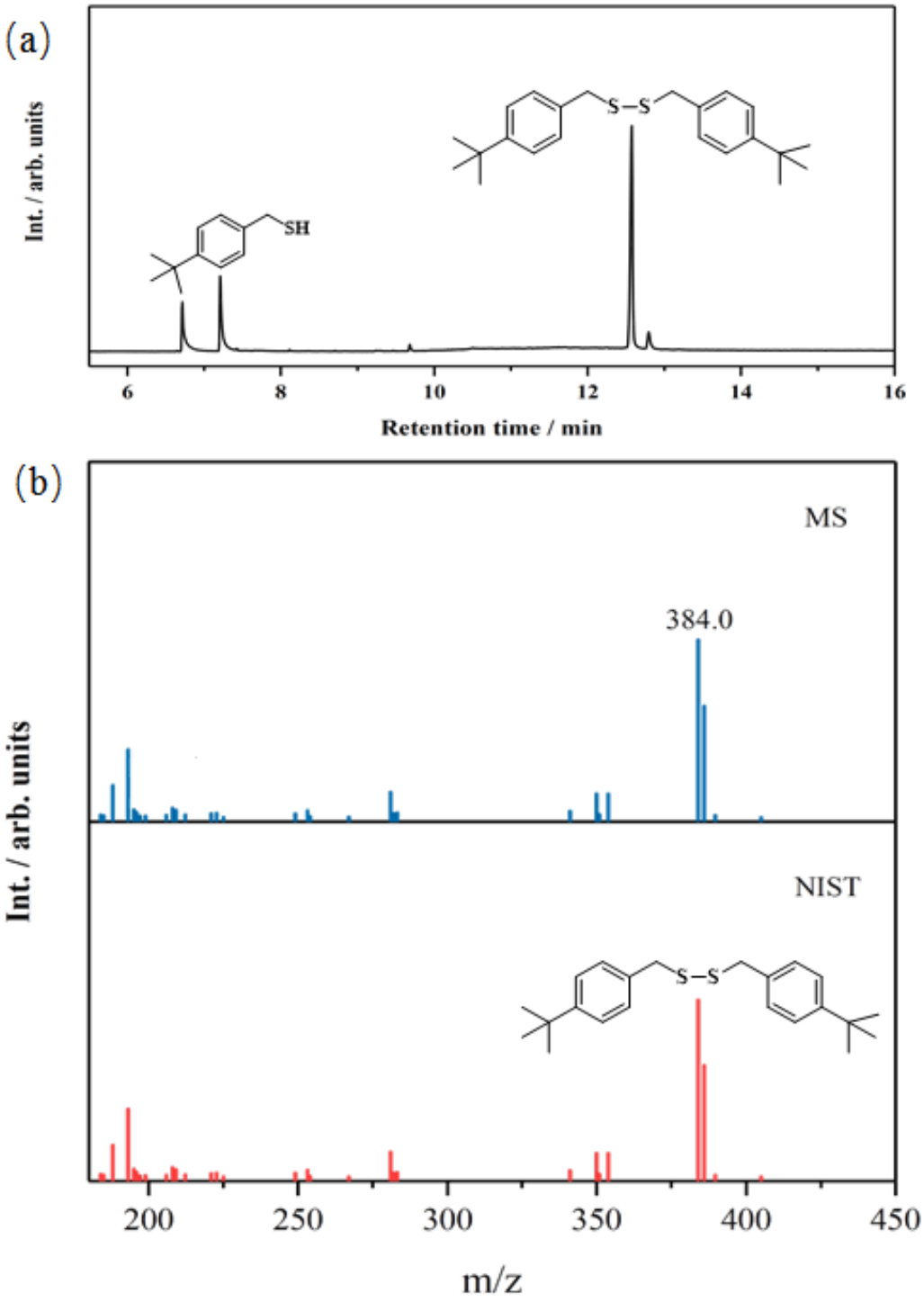

Fig. S5. (a) GC spectrum of 1,2-bis(4-(tert-butyl)benzyl)disulfane. (b) MS spectrum from GC-MS and the NIST database (below).

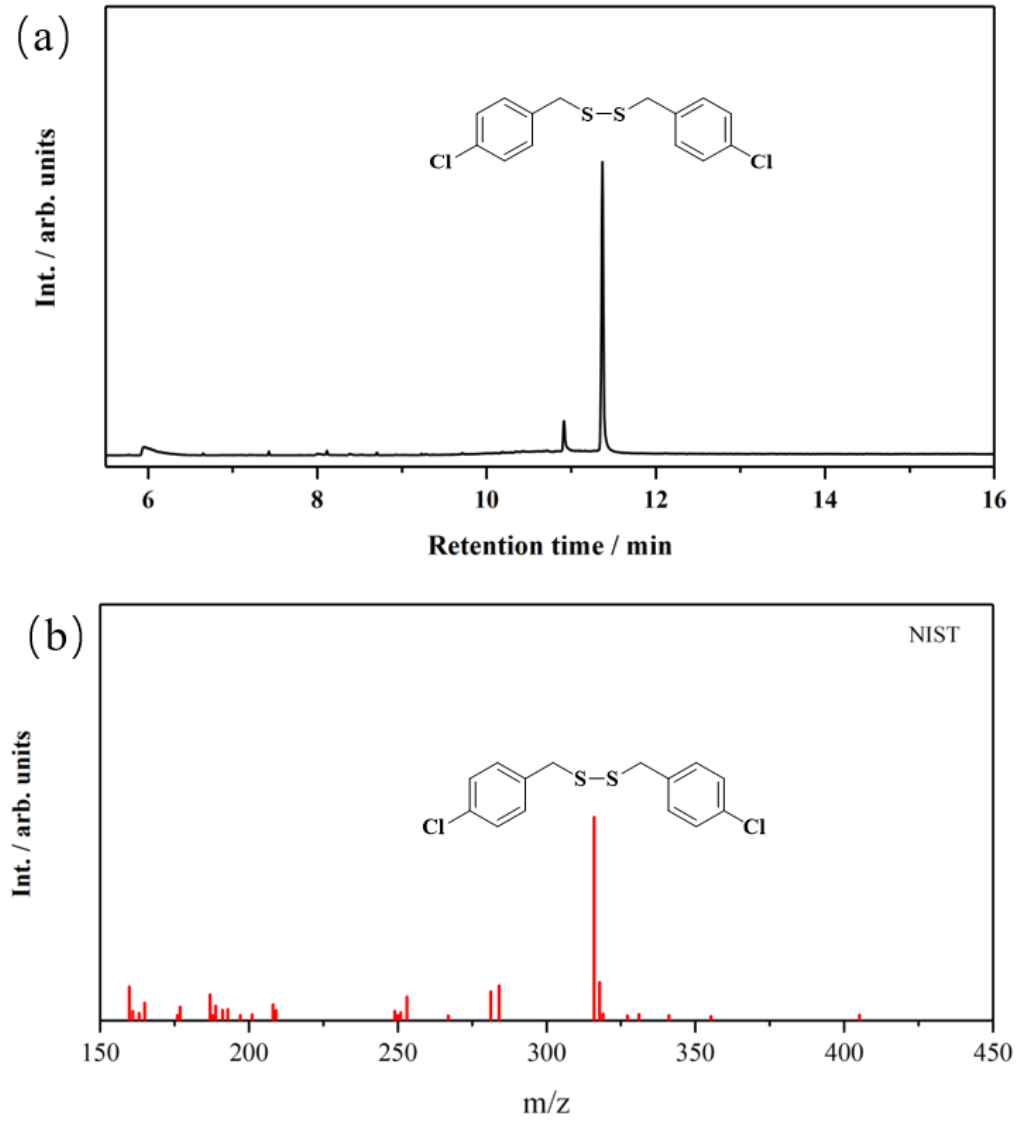

Fig. S6. (a) GC spectrum of 1,2-bis(4-chlorobenzyl)disulfane. (b) MS spectrum from GC-MS and the NIST database (below).

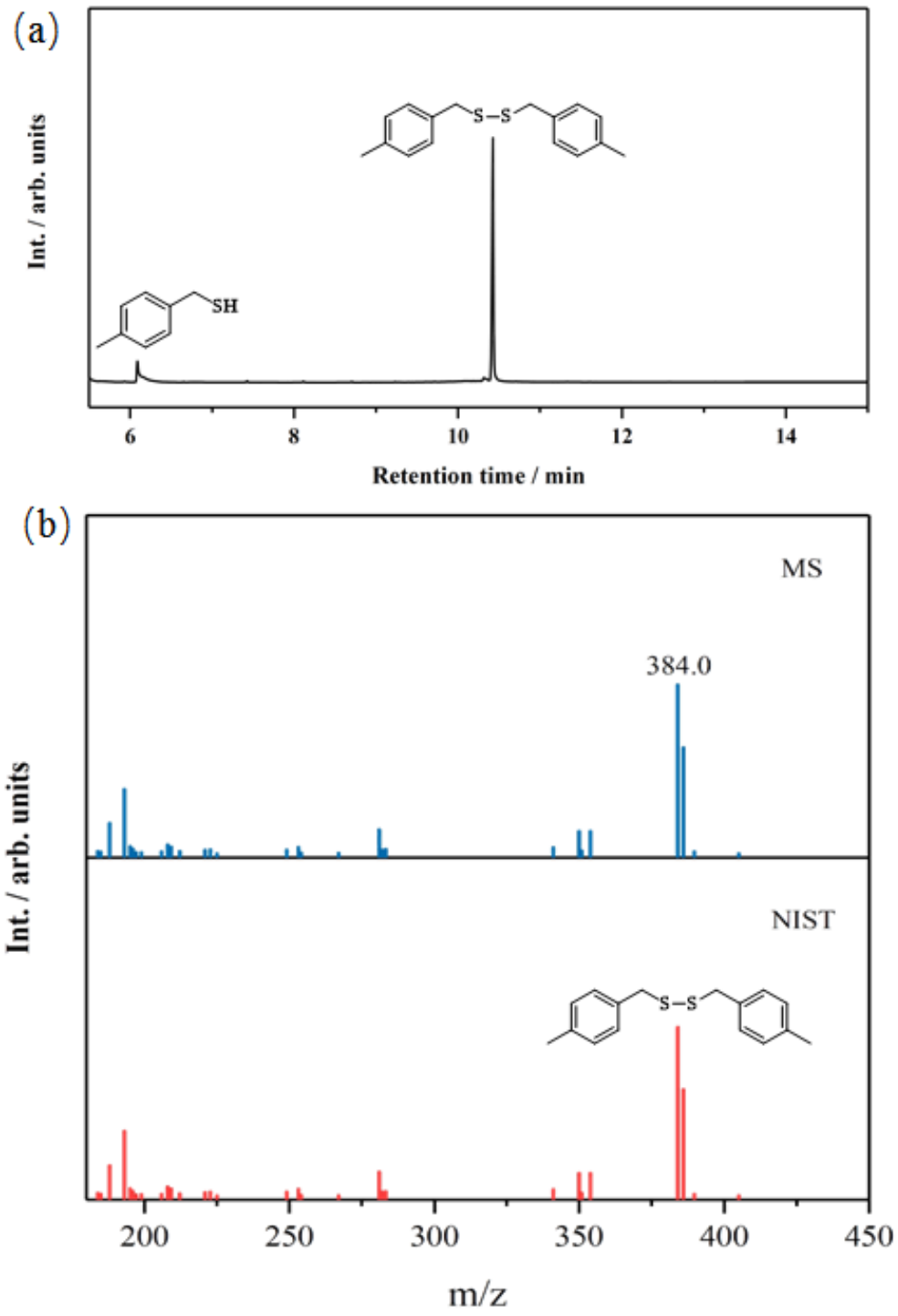

Fig. S7. (a) GC spectrum of 1,2-bis(4-methylbenzyl)disulfane. (b) MS spectrum from GC-MS and the NIST database (below).

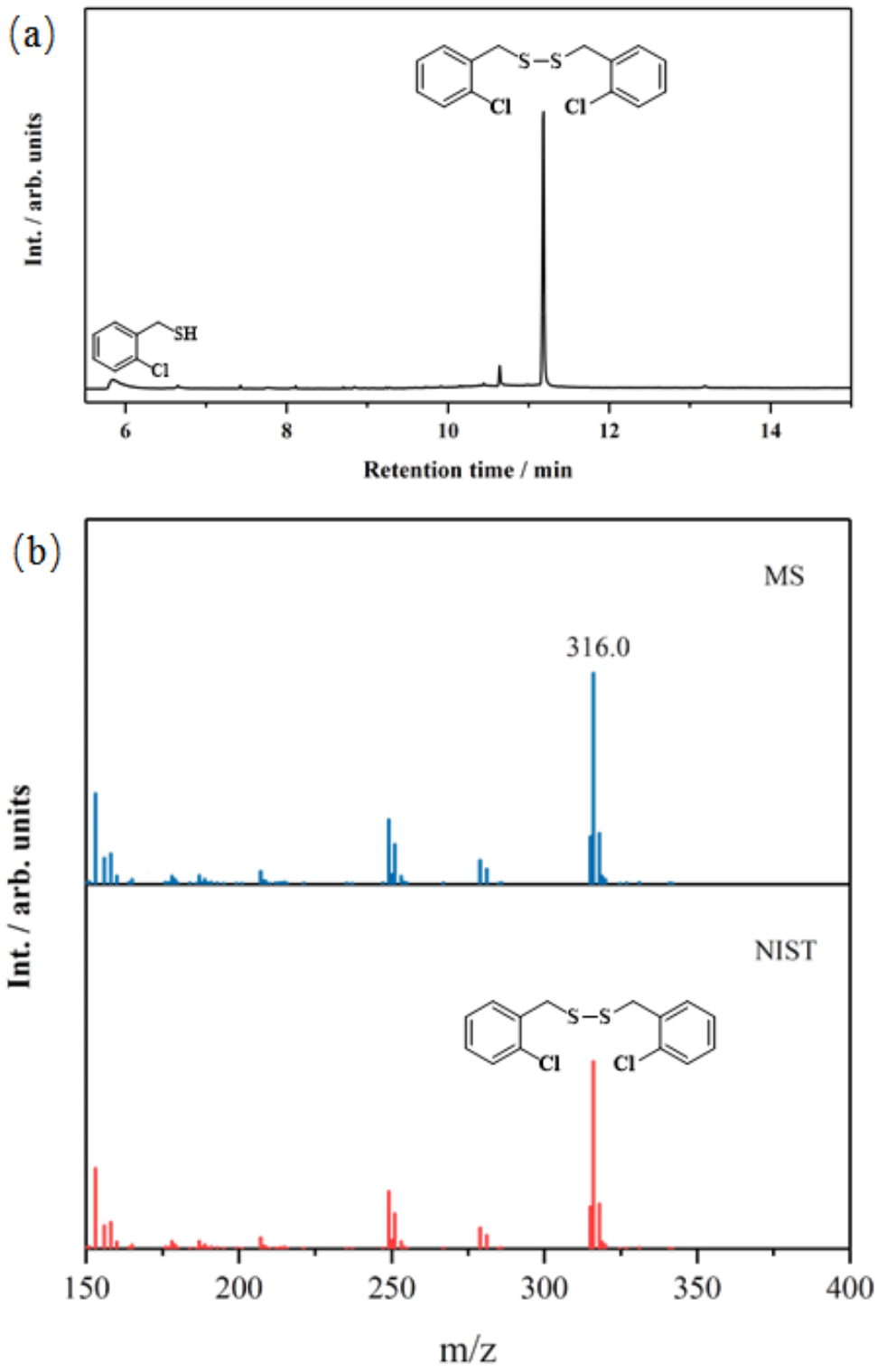

Fig. S8. (a)GC spectrum of 1,2-bis(2-chlorophenyl)disulfane. (b) MS spectrum from GC-MS and the NIST database (below).

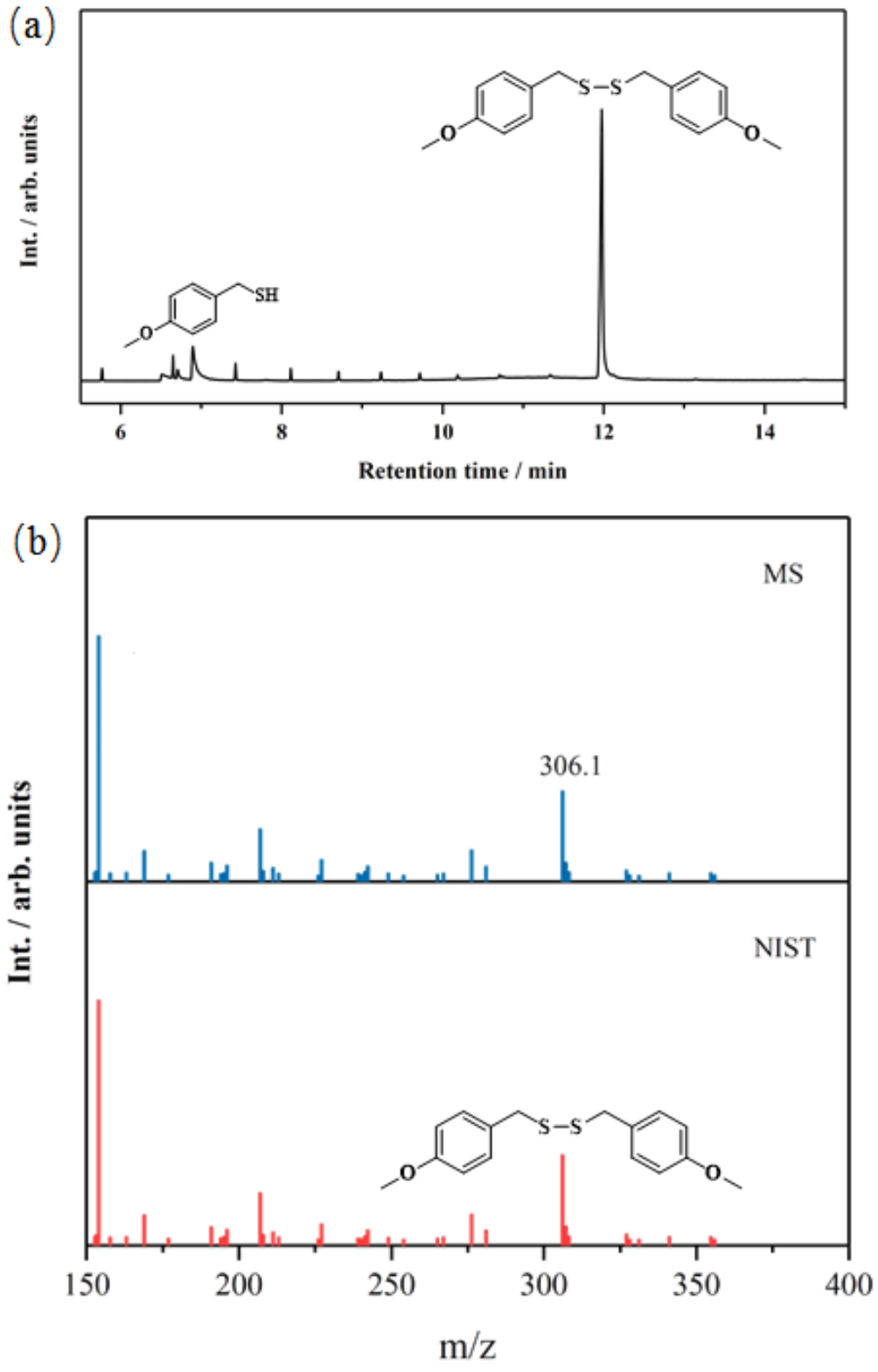

Fig. S9. (a) GC spectrum of 1,2-bis(4-methoxybenzyl)disulfane. (b) MS spectrum from GC-MS and the NIST database (below).

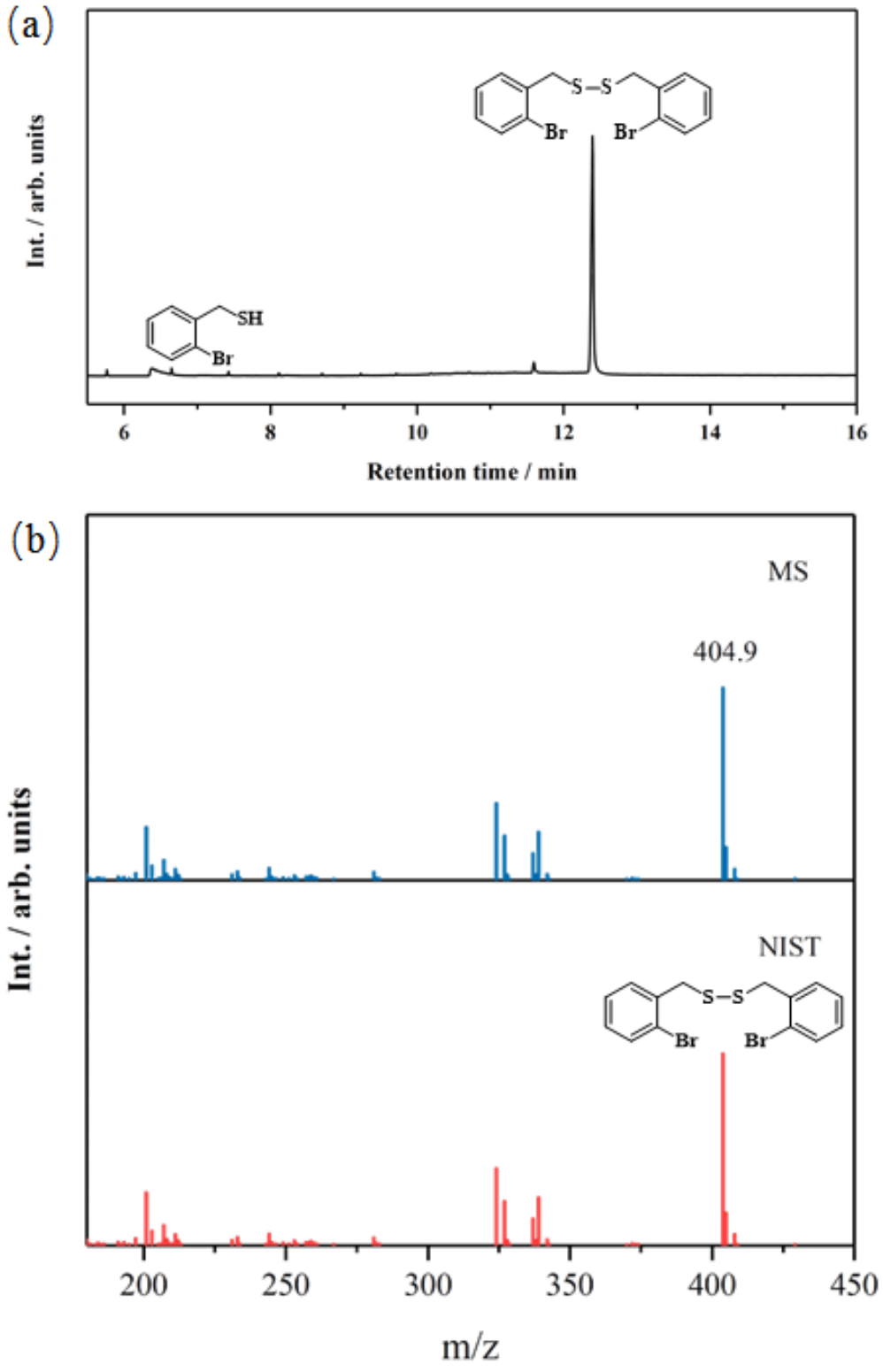

Fig. S10. (a) GC spectrum of 1,2-bis(2-bromobenzyl)disulfane. (b) MS spectrum from GC-MS and the NIST database (below).

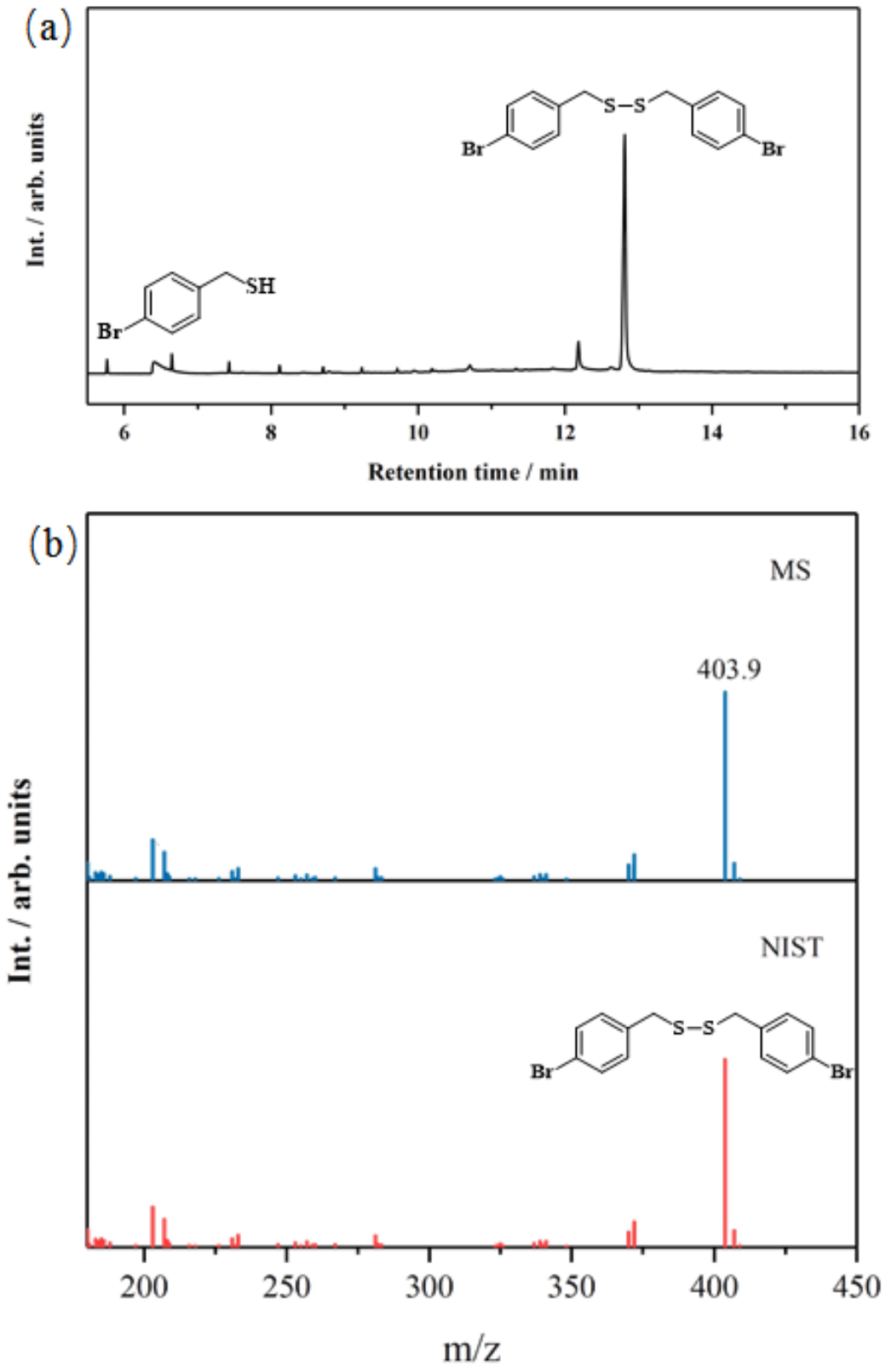

Fig. S11. (a) GC spectrum of 1,2-bis(4-bromobenzyl)disulfane. (b) MS spectrum from GC-MS and the NIST database (below).

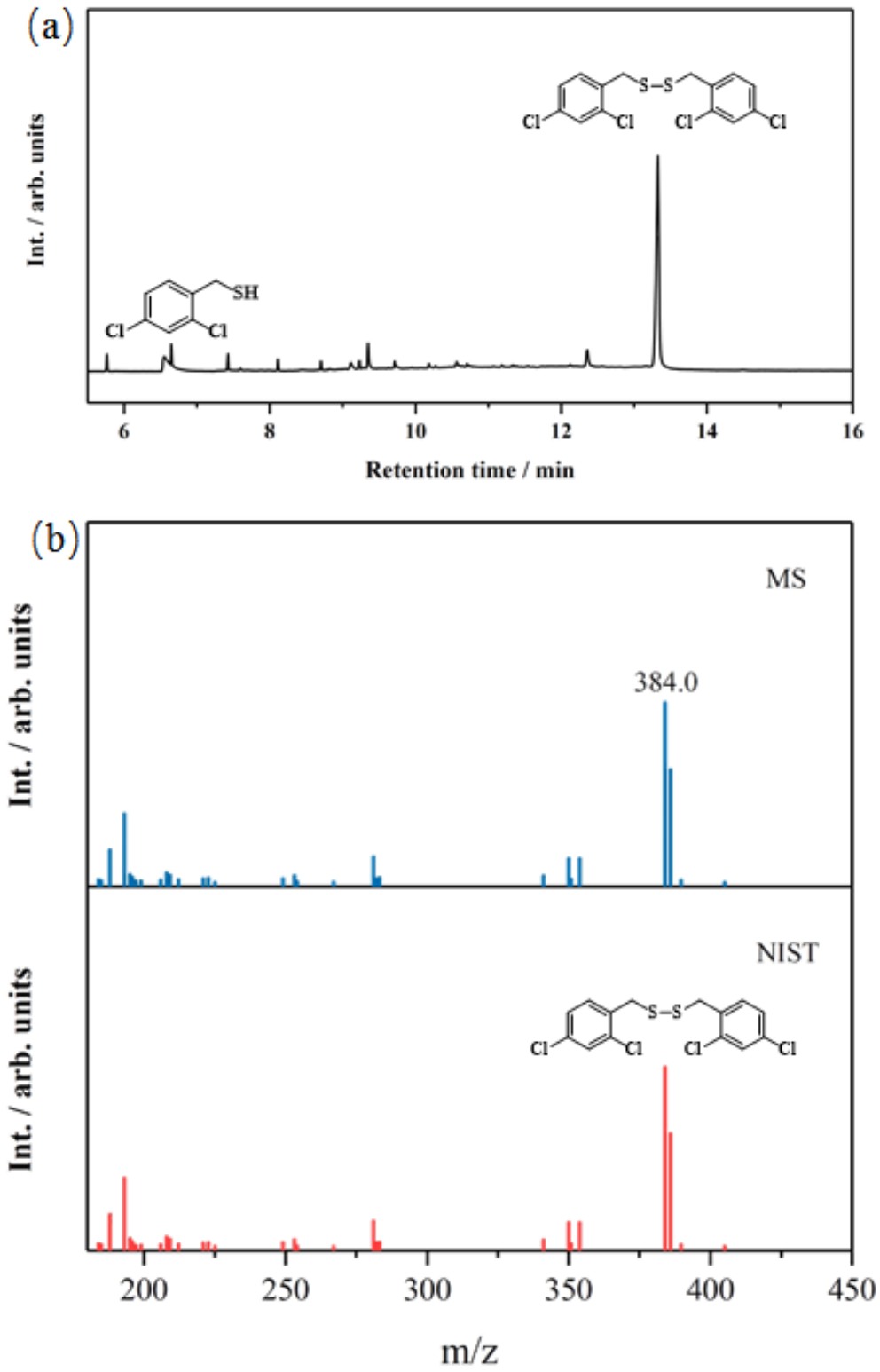

Fig. S12. (a) GC spectrum of 1,2-bis(2,4-dichlorobenzyl)disulfane. (b) MS spectrum from GC-MS and the NIST database (below).

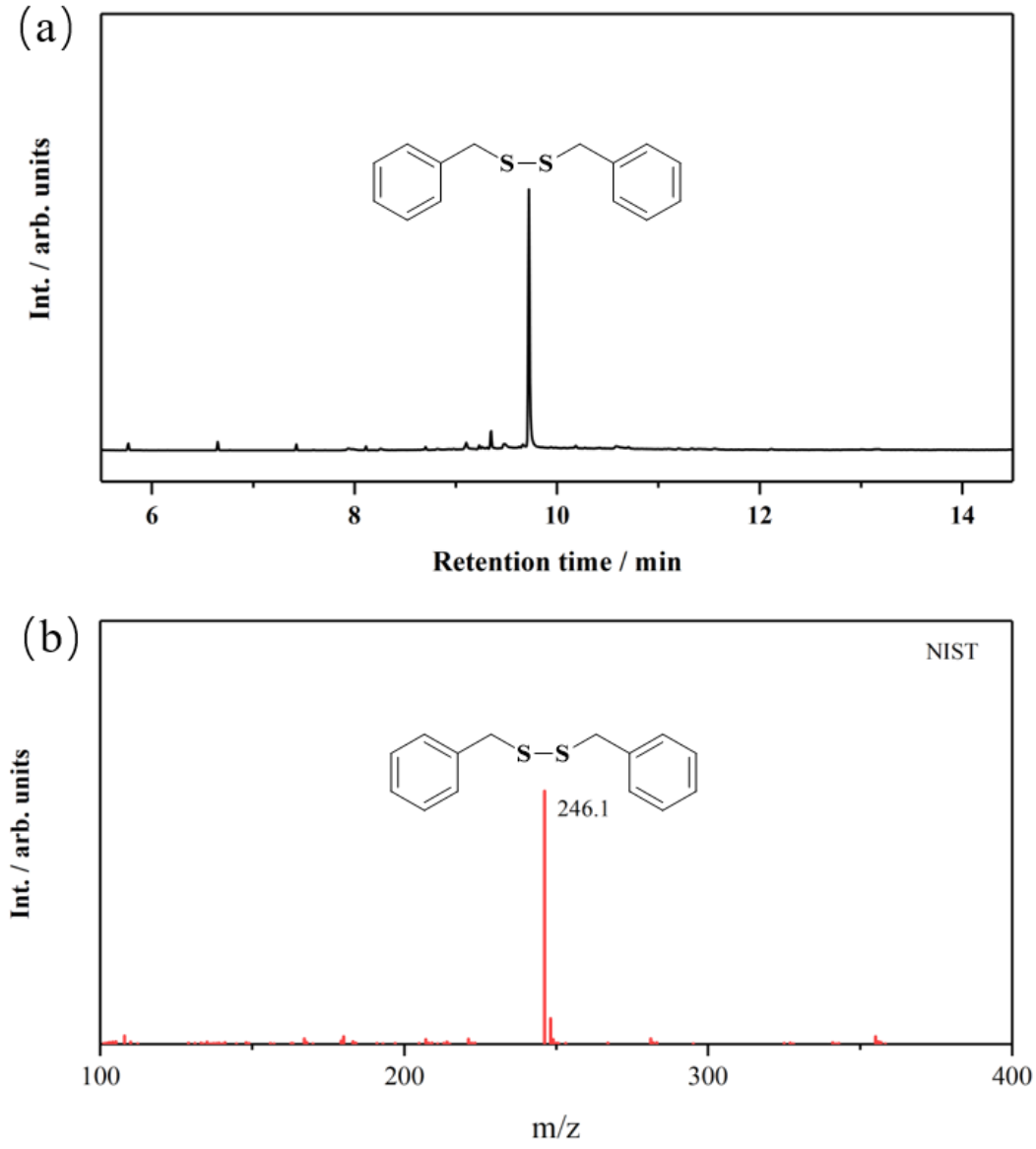

Fig. S13. (a) GC spectrum of 1,2-dibenzyldisulfane. (b) MS spectrum from GC-MS and the NIST database (below).

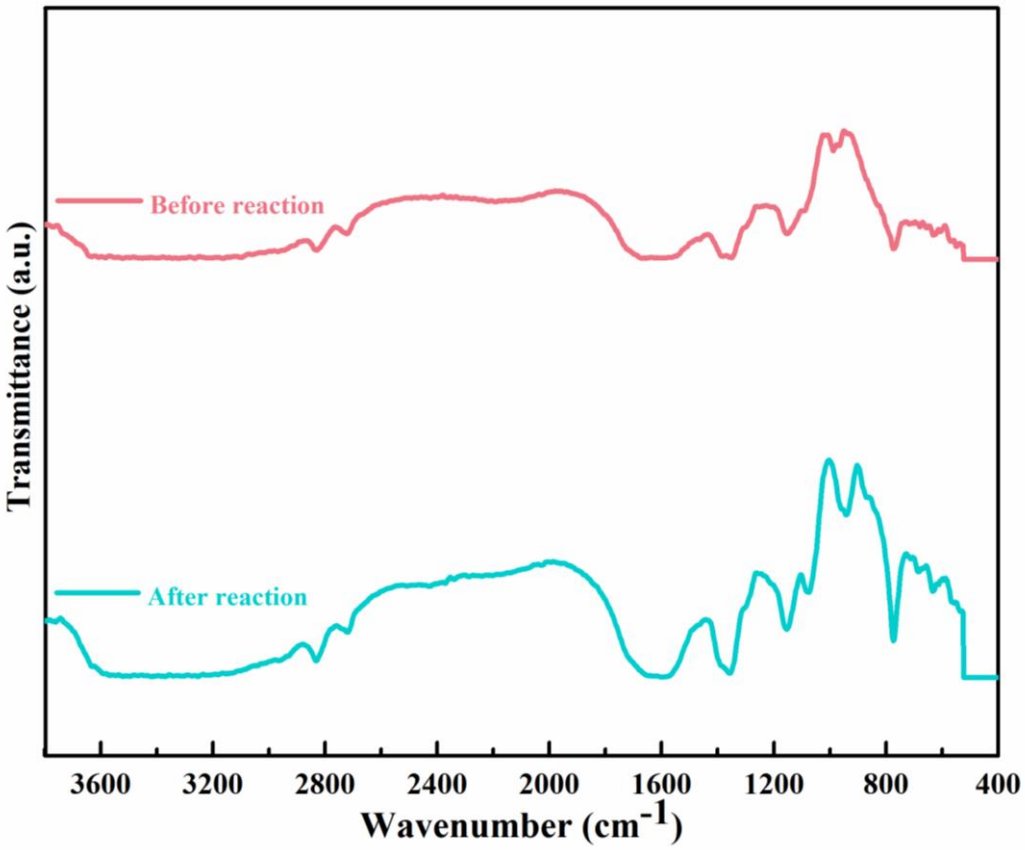

Fig. S14. FT-IR spectra of OBCP sample before and after the stability test.

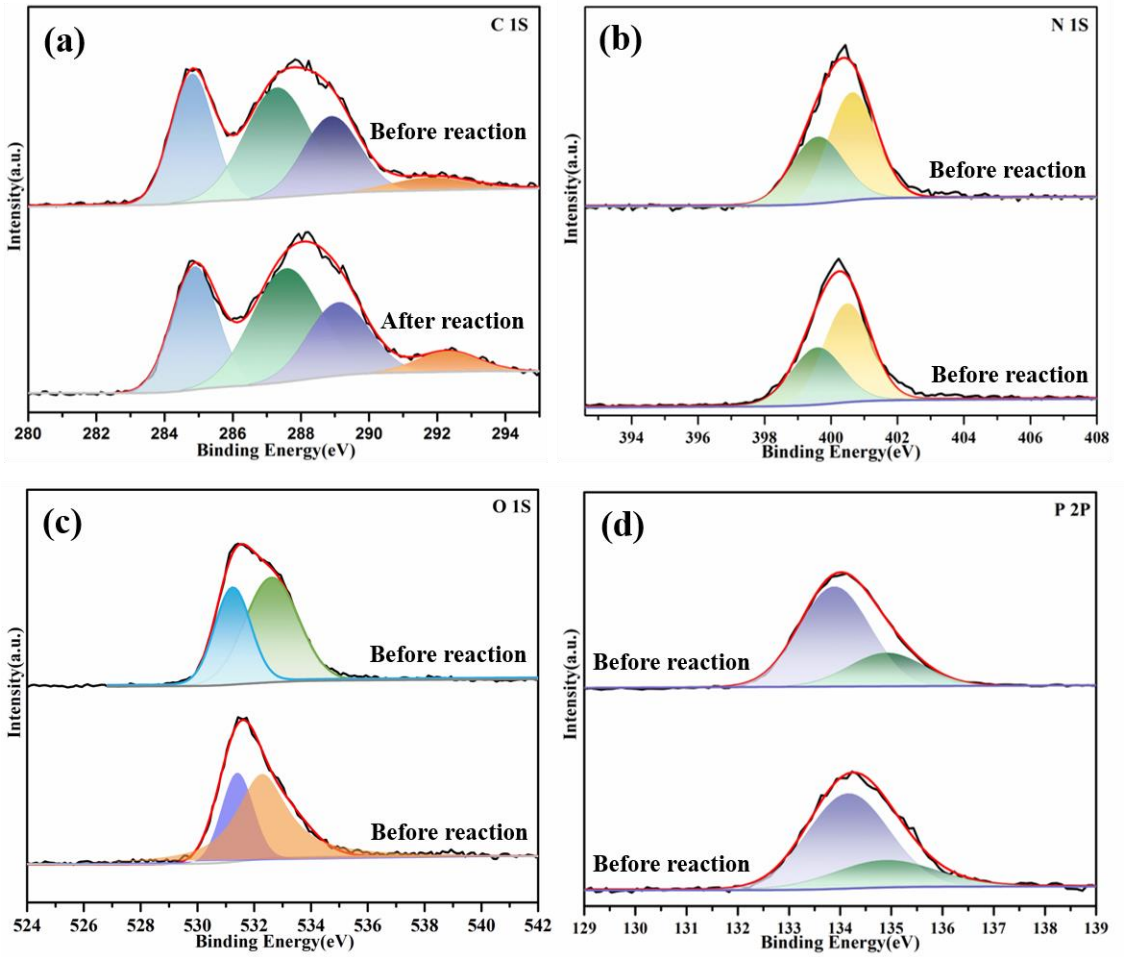

Fig. S15. XPS spectra of OBCP sample before and after the stability test.

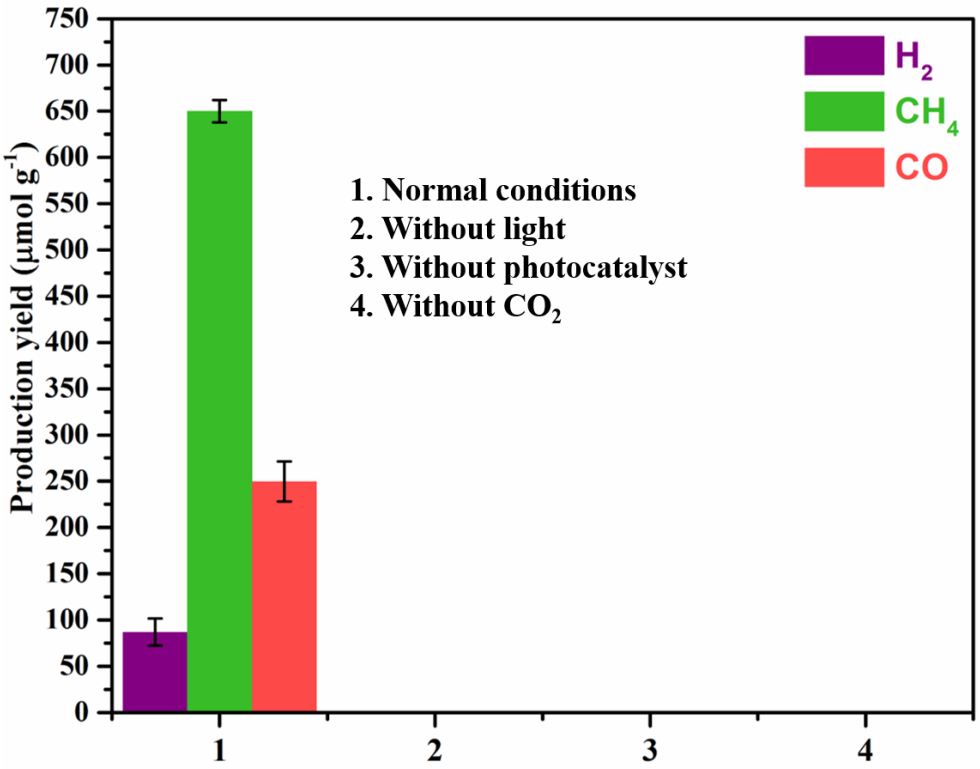

Fig. S16. Control experiments of OBCP sample.

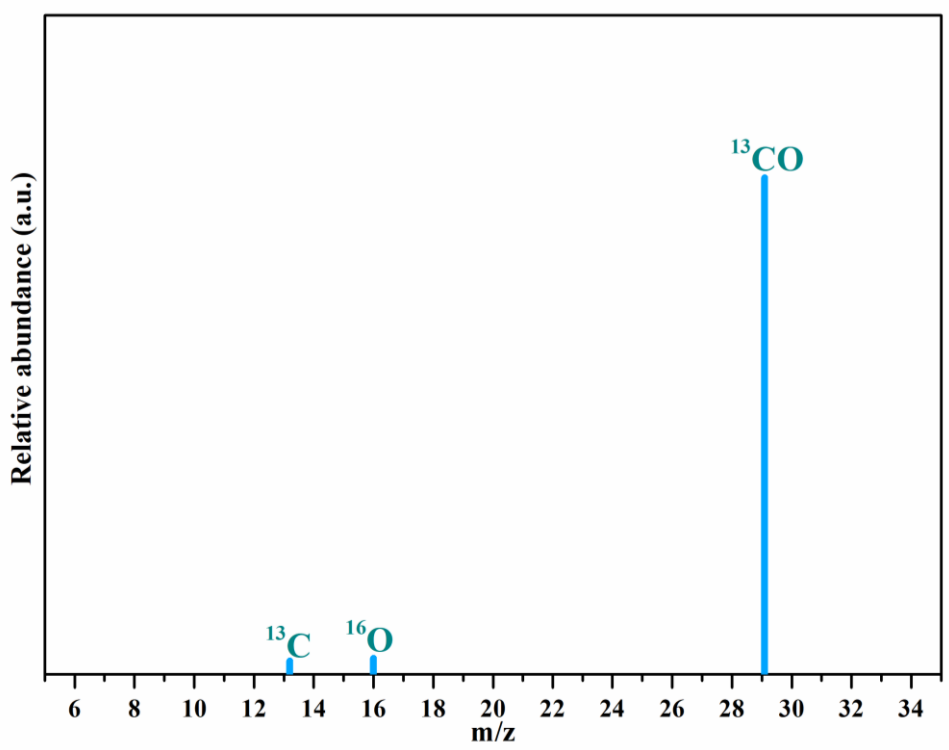

Fig. S17. GC-MS analysis of OBCP.

$$* + CO_2 + e^- + H^+ \rightarrow HCOO^* \quad (1)$$

$$HCOO^* + e^- + H^+ \rightarrow CO^* + H_2O \quad (2)$$

$$CO^* \rightarrow CO + * \quad (3)$$

$$CO^* + e^- + H^+ \rightarrow CHO^* + H_2O \quad (4)$$

$$CHO^* + e^- + H^+ \rightarrow + CH_2O^* \quad (5)$$

$$CH_2O^* + e^- + H^+ \rightarrow CH_3O^* \quad (6)$$

$$CH_3O^* + e^- + H^+ \rightarrow CH_3OH^* \quad (7)$$

$$CH_3OH^* + e^- + H^+ \rightarrow CH_3^* + H_2O \quad (8)$$

$$CH_3^* + e^- + H^+ \rightarrow CH_4 \uparrow + * \quad (9)$$

Fig. S18. Plausible route of photocatalytic CO_2 reduction.

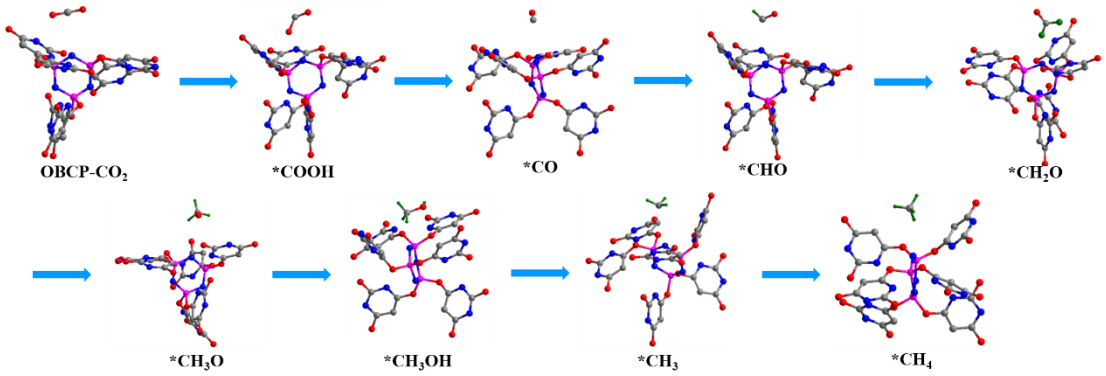

Fig. S19. Reaction pathways associated to photoactivation of CO_2 molecules at OBCP surface.

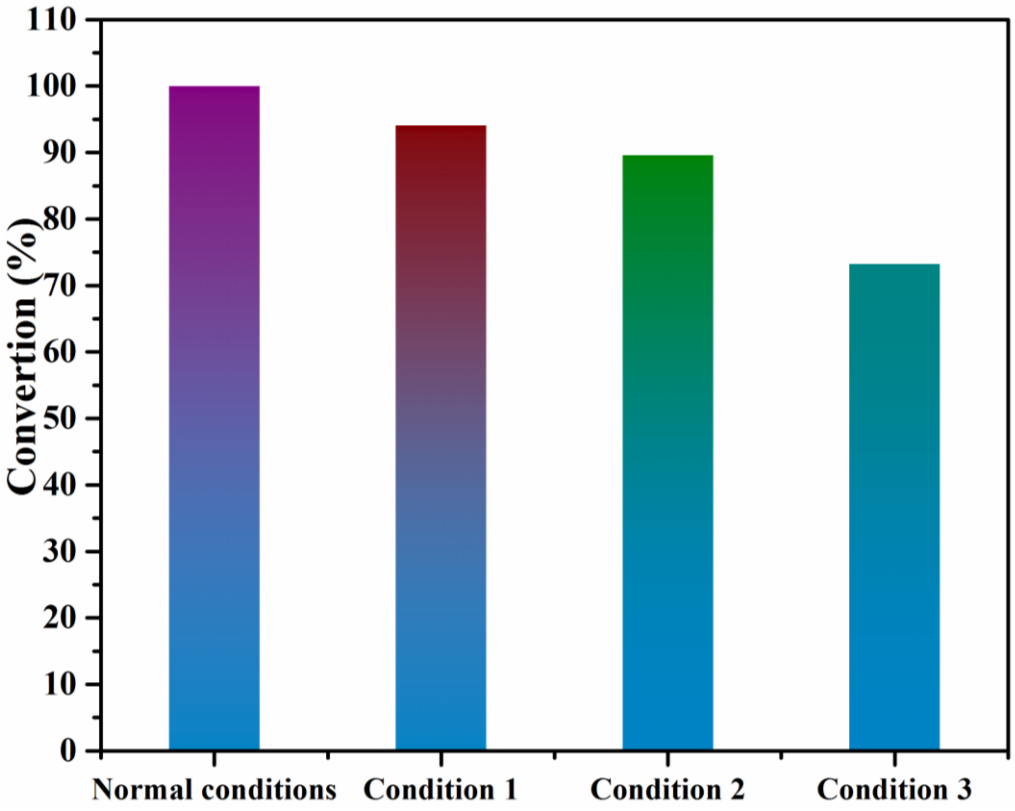

Fig. S20. Free radical trapping experiment of OBCP.

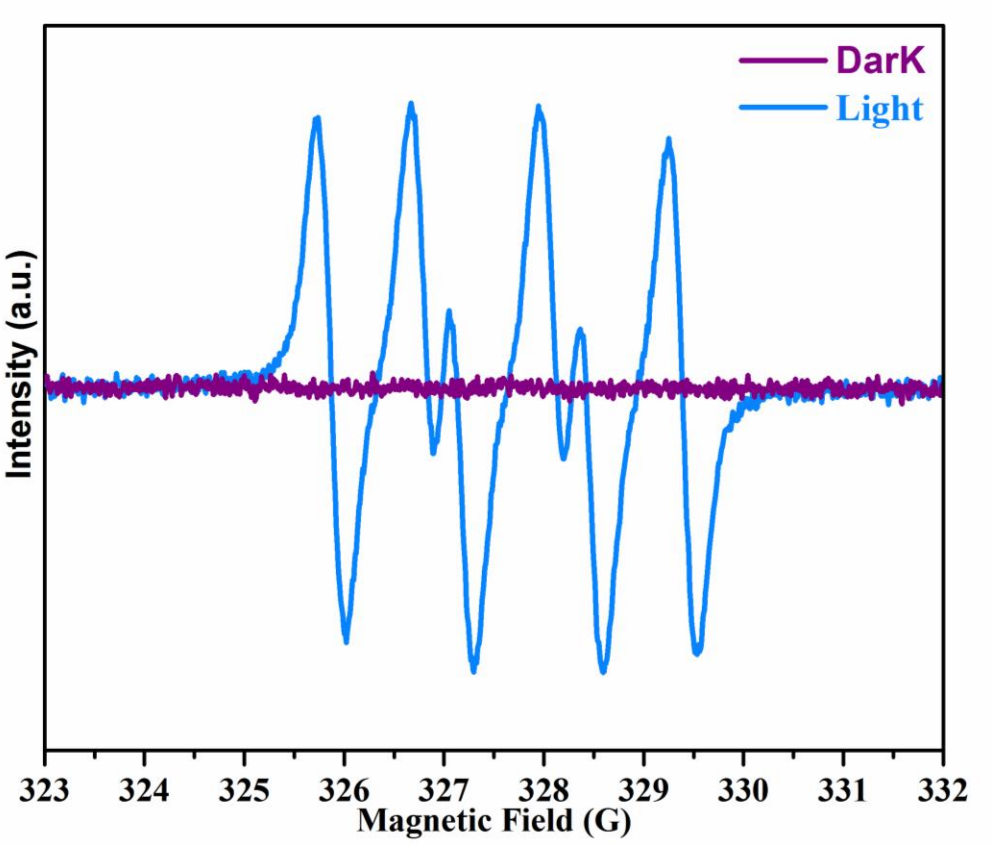

Fig. S21. EPR spectra of $O_2^{\cdot-}$ in OBCP sample.

Computational Details

All computations were performed under the framework of Density Functional Theory (DFT) using the Gaussian 16 or MS software package of programs. In our calculation, the simplest possible repetitive unit consisting of single trithiocyanuric acid and single phosphonitrile was taken into consideration. Molecular geometries were optimized using B3LYP(g) and energy was calculated using B3LYP(g,d).

DFT-optimized geometry of NBCP (singlet).

Atom	x	y	z
P	**9.74840000**	**4.81980000**	**3.13560000**
N	**10.94900000**	**3.77270000**	**3.00150000**
P	**12.48840000**	**4.23310000**	**2.88680000**
N	**12.78660000**	**5.79850000**	**3.03790000**
P	**11.62530000**	**6.87980000**	**3.06170000**
N	**10.10750000**	**6.39080000**	**3.04030000**
N	**13.17080000**	**3.77400000**	**1.50430000**
N	**13.35020000**	**3.34470000**	**3.92920000**
P	**9.47940000**	**13.32820000**	**3.03060000**
N	**10.72660000**	**12.32560000**	**3.19730000**
P	**12.22570000**	**12.86860000**	**3.18810000**
N	**12.48300000**	**14.43370000**	**3.24070000**
P	**11.26560000**	**15.47640000**	**3.13550000**
N	**9.76820000**	**14.89340000**	**3.22610000**
O	**13.06980000**	**12.31520000**	**1.87900000**
O	**13.06790000**	**12.25750000**	**4.46990000**
C	**13.35620000**	**10.98410000**	**1.66600000**
C	**13.36050000**	**10.92140000**	**4.63290000**
N	**12.33840000**	**10.12450000**	**1.59890000**
C	**12.74100000**	**8.84740000**	**1.62620000**
N	**13.99490000**	**8.39750000**	**1.60540000**
C	**14.90230000**	**9.38070000**	**1.66190000**
N	**14.66180000**	**10.69370000**	**1.64340000**
N	**12.34830000**	**10.05110000**	**4.63730000**
C	**12.76090000**	**8.77750000**	**4.58460000**
N	**14.01790000**	**8.33640000**	**4.61710000**
C	**14.91610000**	**9.32960000**	**4.61870000**
N	**14.66780000**	**10.64000000**	**4.68700000**
O	**11.75390000**	**7.85970000**	**4.38330000**
N	**16.22020000**	**8.93080000**	**4.43470000**
O	**11.72250000**	**7.93580000**	**1.79340000**
N	**16.19630000**	**8.95620000**	**1.84990000**

P	**17.13280000**	**9.39780000**	**3.13710000**
N	**18.37750000**	**8.41520000**	**3.13510000**
P	**19.87840000**	**8.98320000**	**3.05960000**
N	**20.09190000**	**10.56700000**	**3.25540000**
P	**18.86560000**	**11.59010000**	**3.11120000**
N	**17.38180000**	**10.97090000**	**3.17180000**
O	**20.47990000**	**8.42370000**	**1.67550000**
O	**20.84310000**	**8.23650000**	**4.12170000**
O	**18.92350000**	**12.75060000**	**4.23880000**
O	**19.14090000**	**12.43100000**	**1.76470000**
O	**8.73570000**	**13.18250000**	**1.60800000**
O	**8.33370000**	**12.80760000**	**4.04880000**
O	**8.99440000**	**4.43800000**	**4.50910000**
H	**18.20860000**	**12.58900000**	**4.89360000**
H	**20.85290000**	**8.73260000**	**4.96900000**
H	**21.40560000**	**8.73070000**	**1.55300000**
H	**8.76090000**	**12.29390000**	**4.76950000**
H	**8.54870000**	**12.23670000**	**1.41240000**
H	**18.43890000**	**13.10690000**	**1.62870000**
H	**13.19310000**	**2.79400000**	**1.43420000**
H	**12.85590000**	**3.23940000**	**4.77150000**
H	**8.17970000**	**4.97720000**	**4.61840000**
O	**8.55250000**	**4.54690000**	**2.07650000**
H	**8.70050000**	**5.07940000**	**1.26420000**
N	**11.54430000**	**16.32350000**	**1.79480000**
H	**10.84680000**	**17.00460000**	**1.66760000**
N	**11.38860000**	**16.64500000**	**4.24860000**
H	**10.88920000**	**16.38930000**	**5.05450000**
H	**12.33950000**	**16.81610000**	**1.19730000**
H	**12.13740000**	**17.44650000**	**4.07790000**
H	**14.38870000**	**3.17350000**	**3.57660000**
H	**14.07080000**	**4.12360000**	**0.95660000**
H	**16.88180000**	**8.39980000**	**5.15060000**
H	**16.90660000**	**8.68140000**	**1.04240000**

DFT-optimized geometry of OBCP (singlet).

Atom	x	y	z
P	**9.74620000**	**4.82110000**	**3.13530000**
N	**10.94600000**	**3.77290000**	**3.00530000**

P	12.48580000	4.23160000	2.89080000
N	12.78540000	5.79700000	3.03970000
P	11.62500000	6.87890000	3.06090000
N	10.10710000	6.39180000	3.03810000
O	13.16840000	3.76980000	1.50940000
O	13.34630000	3.34390000	3.93480000
P	9.48050000	13.32680000	3.03360000
N	10.72840000	12.32440000	3.19750000
P	12.22700000	12.86810000	3.18780000
N	12.48410000	14.43290000	3.23960000
P	11.26620000	15.47540000	3.13700000
N	9.76930000	14.89180000	3.22930000
O	13.07170000	12.31390000	1.87930000
O	13.06980000	12.25770000	4.46990000
C	13.35800000	10.98330000	1.66650000
C	13.36170000	10.92200000	4.63380000
N	12.34020000	10.12330000	1.60020000
C	12.74290000	8.84580000	1.62590000
N	13.99700000	8.39640000	1.60250000
C	14.90480000	9.37980000	1.65400000
N	14.66370000	10.69280000	1.63720000
N	12.34910000	10.05190000	4.63770000
C	12.76030000	8.77770000	4.58180000
N	14.01740000	8.33570000	4.61220000
C	14.91660000	9.32830000	4.60980000
N	14.66890000	10.63900000	4.68190000
O	11.75280000	7.86110000	4.38150000
O	16.21960000	8.92840000	4.42530000
O	11.72490000	7.93390000	1.79190000
O	16.19910000	8.95650000	1.84100000
P	17.13420000	9.39790000	3.12950000
N	18.37930000	8.41640000	3.12820000
P	19.88010000	8.98590000	3.06080000
N	20.09100000	10.56960000	3.25890000
P	18.86470000	11.59170000	3.11050000
N	17.38120000	10.97100000	3.16500000
O	20.48900000	8.42830000	1.67920000
O	20.84000000	8.23910000	4.12700000
O	18.91760000	12.75160000	4.23880000
O	19.14400000	12.43340000	1.76550000
O	8.73440000	13.18130000	1.61240000
O	8.33670000	12.80560000	4.05350000
O	8.98920000	4.44250000	4.50800000
H	18.19980000	12.58970000	4.89150000

H	**20.84610000**	**8.73510000**	**4.97520000**
H	**21.41580000**	**8.73610000**	**1.56140000**
H	**8.76480000**	**12.29070000**	**4.77380000**
H	**8.54540000**	**12.23520000**	**1.41710000**
H	**18.44210000**	**13.10970000**	**1.62680000**
H	**13.19020000**	**2.78900000**	**1.44010000**
H	**12.85150000**	**3.23990000**	**4.77770000**
H	**8.17310000**	**4.98140000**	**4.61440000**
O	**8.55210000**	**4.54760000**	**2.07450000**
H	**8.70110000**	**5.07980000**	**1.26140000**
O	**11.54270000**	**16.32360000**	**1.79660000**
H	**10.84490000**	**17.00550000**	**1.67050000**
O	**11.39060000**	**16.64310000**	**4.25080000**
H	**10.89170000**	**16.38720000**	**5.05770000**

DFT-optimized geometry of SBCP (singlet).

Atom	x	y	z
P	**9.46270000**	**4.78450000**	**3.11350000**
N	**10.61710000**	**3.67480000**	**3.05020000**
P	**12.18000000**	**4.07440000**	**2.99350000**
N	**12.54890000**	**5.64350000**	**3.07400000**
P	**11.42570000**	**6.76930000**	**3.04360000**
N	**9.89360000**	**6.33530000**	**3.00170000**
S	**13.14320000**	**3.42300000**	**1.23310000**
S	**13.19540000**	**2.95130000**	**4.46210000**
P	**9.75330000**	**13.43000000**	**3.04910000**
N	**10.90860000**	**12.31620000**	**3.15640000**
P	**12.45070000**	**12.71070000**	**3.14520000**
N	**12.85520000**	**14.25000000**	**3.16270000**
P	**11.72400000**	**15.41080000**	**3.16400000**
N	**10.17940000**	**14.96220000**	**3.28110000**
O	**13.25150000**	**12.07350000**	**1.85080000**
O	**13.24470000**	**12.05130000**	**4.43160000**
C	**13.42480000**	**10.72630000**	**1.61090000**
C	**13.42300000**	**10.69690000**	**4.61640000**
N	**12.34850000**	**9.93620000**	**1.62970000**
C	**12.66520000**	**8.63410000**	**1.57220000**
N	**13.87250000**	**8.10640000**	**1.40460000**
C	**14.86260000**	**9.02510000**	**1.34850000**
N	**14.69240000**	**10.35780000**	**1.41940000**

N	**12.33960000**	**9.91720000**	**4.59710000**
C	**12.64880000**	**8.61320000**	**4.55020000**
N	**13.85860000**	**8.07150000**	**4.63420000**
C	**14.85630000**	**8.97690000**	**4.73470000**
N	**14.69460000**	**10.31480000**	**4.75230000**
O	**11.56880000**	**7.78280000**	**4.33350000**
S	**16.50940000**	**8.30000000**	**4.75060000**
O	**11.59560000**	**7.78050000**	**1.75330000**
S	**16.52170000**	**8.36380000**	**1.27590000**
P	**17.41980000**	**9.25180000**	**3.03250000**
N	**18.91280000**	**8.65250000**	**3.05630000**
P	**20.18380000**	**9.64080000**	**3.06850000**
N	**19.91830000**	**11.20920000**	**3.30890000**
P	**18.46190000**	**11.85130000**	**3.11340000**
N	**17.21330000**	**10.83720000**	**3.06880000**
O	**20.97810000**	**9.32090000**	**1.70340000**
O	**21.28280000**	**9.18090000**	**4.16470000**
O	**18.12660000**	**12.92930000**	**4.27180000**
O	**18.55970000**	**12.77760000**	**1.79960000**
O	**8.96940000**	**13.39420000**	**1.64220000**
O	**8.59000000**	**12.98770000**	**4.08180000**
O	**8.64200000**	**4.46600000**	**4.46300000**
H	**17.40300000**	**12.56720000**	**4.83380000**
H	**21.13990000**	**9.67710000**	**5.00120000**
H	**21.79370000**	**9.86830000**	**1.64090000**
H	**8.98310000**	**12.41800000**	**4.78100000**
H	**8.66450000**	**12.48090000**	**1.43620000**
H	**17.69610000**	**13.21550000**	**1.61850000**
H	**12.68940000**	**2.14560000**	**1.37850000**
H	**12.16180000**	**3.07010000**	**5.34430000**
H	**7.84240000**	**5.03570000**	**4.52920000**
O	**8.30110000**	**4.53930000**	**2.01180000**
H	**8.49460000**	**5.06000000**	**1.20040000**
S	**12.19030000**	**16.51470000**	**1.42510000**
H	**11.13530000**	**17.35910000**	**1.60630000**
S	**12.06990000**	**16.85240000**	**4.66340000**
H	**11.27720000**	**16.19400000**	**5.55710000**
