**Electronic supplementary information (ESI)**

# Full-capped 12-S-atom TTP derivatives (BV-TTP, BE-TTP, EM-TTP and EV-TTP):   Syntheses, Structures and charge transport properties

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[a] *State Key Laboratory of Crystal Materials, Shandong University, 250100 Jinan, P. R. China. Fax: +86 531 88362782; Tel: +86 531 88363497;   E-mail:   fangqi@sdu.edu.cn*
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**Contents**

1. $^1$H NMR spectra of BE-TTF, **BE-TTP**, **EM-TTP**, **EV-TTP**, **BV-TTP**, and BV-TTF (Fig. 7).



**Fig.7a** BE-TTF in CDCl$_3$ /TMS



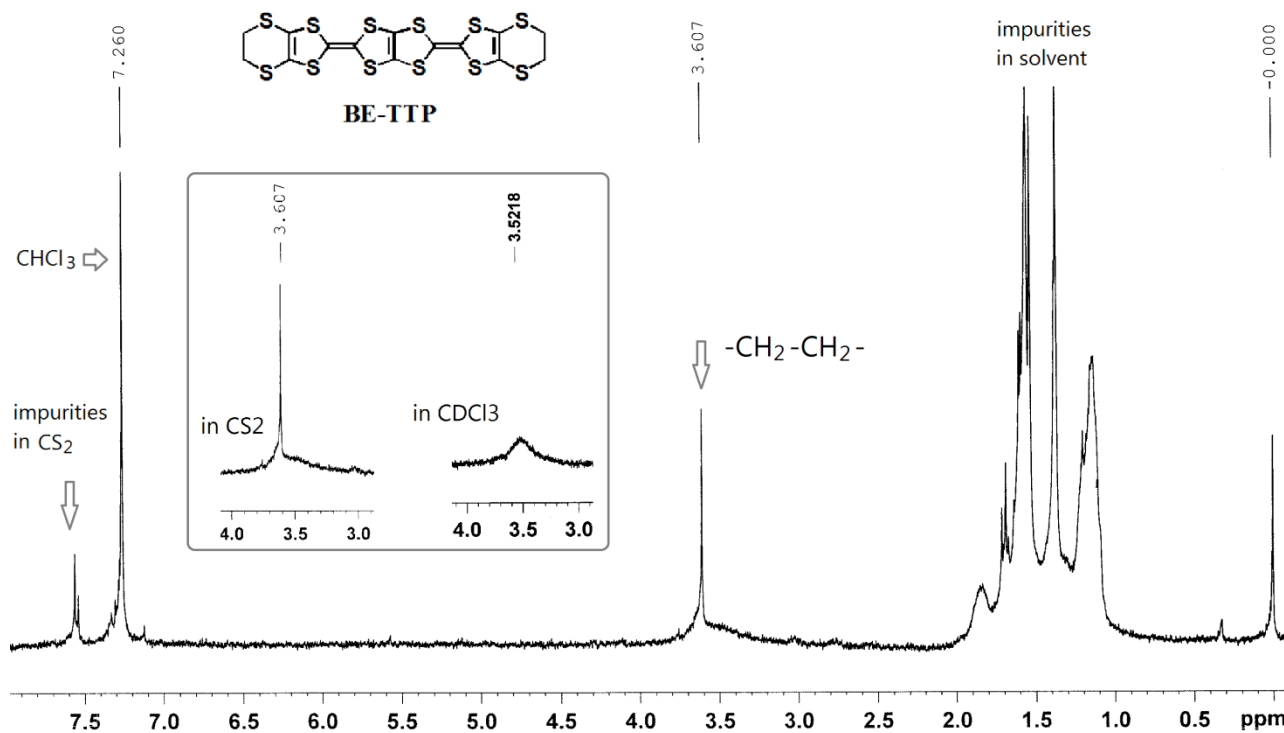**Fig. 7b** **BE-TTP** in CS$_2$, with CDCl$_3$ /TMS external reference. The inset is a comparison of the spectrum from CS$_2$ solution and that from CDCl$_3$ solution

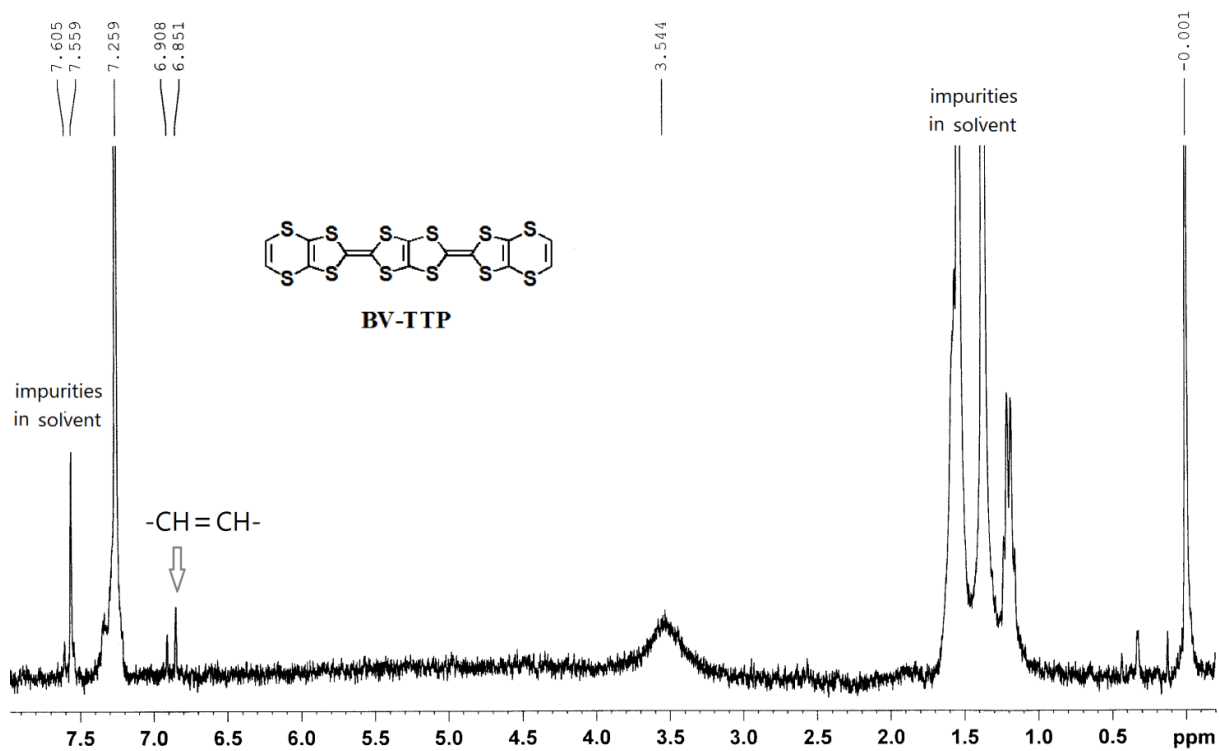**Fig.7c    EM-TTP** in CS$_2$, with CDCl$_3$ /TMS external reference.



**Fig.7d    EV-TTP** in CS$_2$, with CDCl$_3$ /TMS external reference

**Fig. 7e**  **BV-TTP** in CS$_2$, with CDCl$_3$ /TMS external reference.
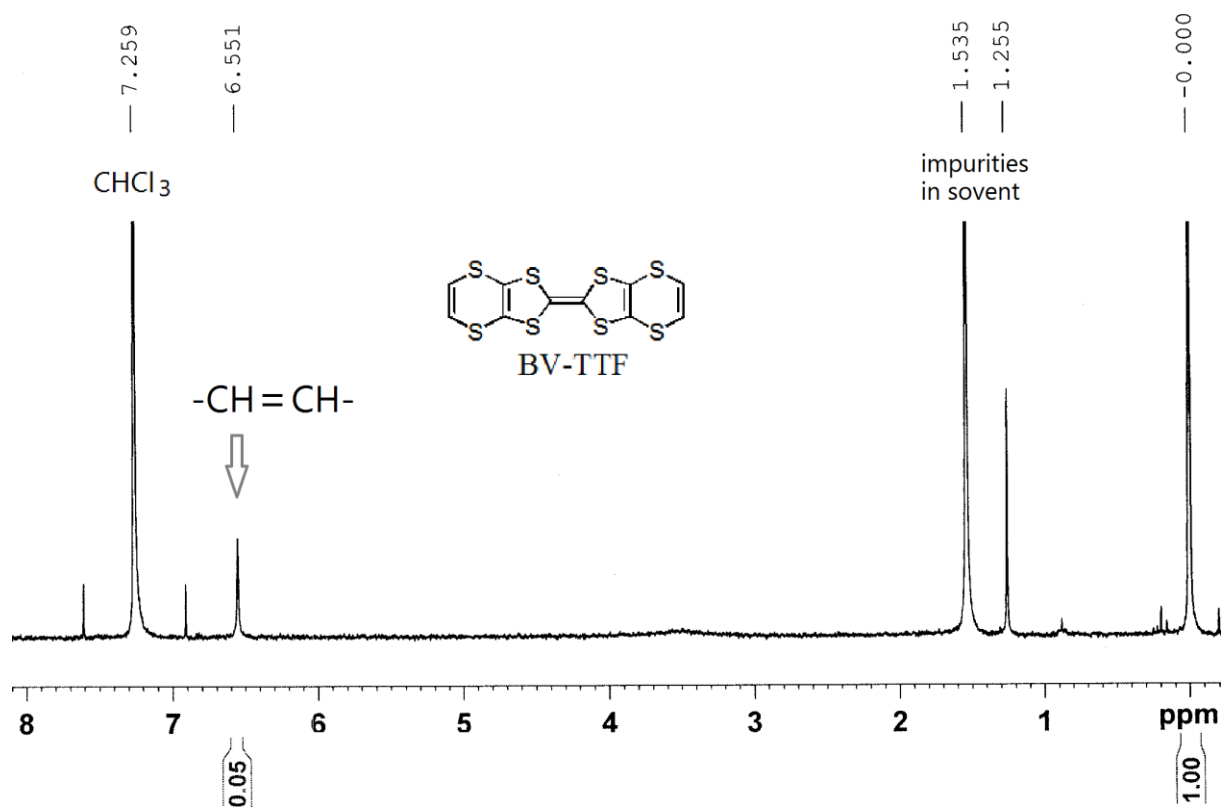


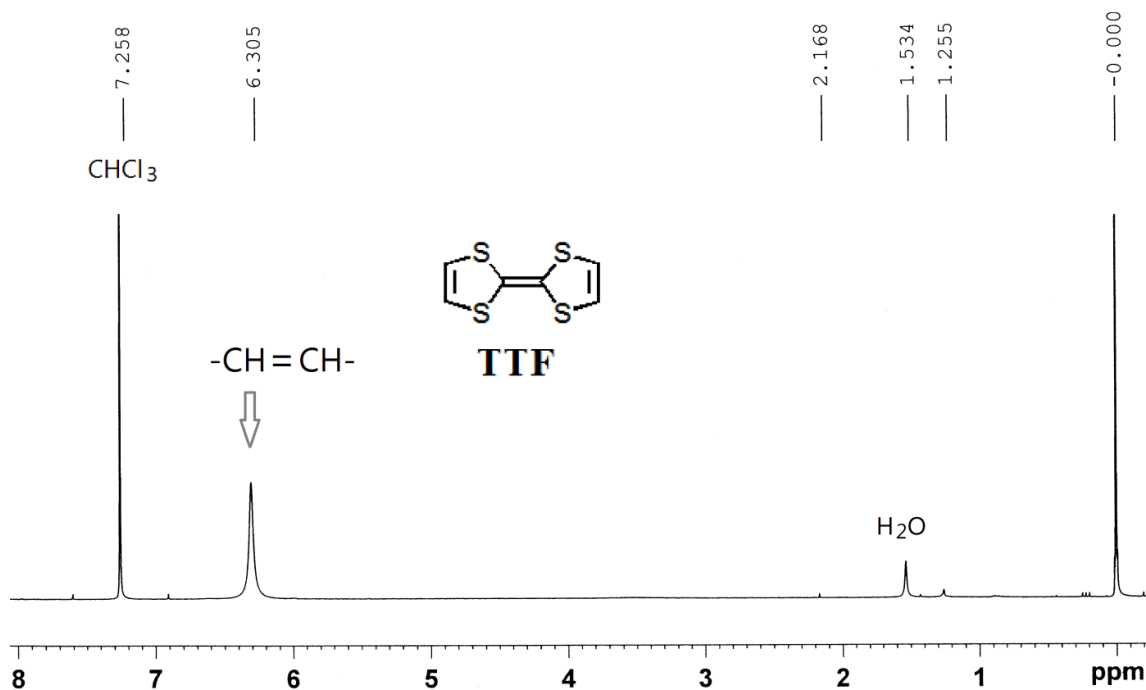**Fig. 7f**  BV-TTF in CDCl$_3$ /TMS.

**Fig. 7g** TTF in CDCl$_3$ /TMS

**Fig. 7** $^1$H NMR spectra of BE-TTF, **BE-TTP**, **EM-TTP**, **EV-TTP**, **BV-TTP**, BV-TTF, and TTF. Because of the extreme low solubility of the full-capped 12-S-atom TTP derivatives in deutero reagents, CS$_2$ had to be used as the solvent. CDCl$_3$/TMS, which is in a capillary and in the NMR tube, was used as the external references. The spectra of BE-TTF, BV-TTF, and TTF are normally in CDCl$_3$/TMS.

## 2. A discussion about electronic donating and π-conjugation of the title TTP derivatives.

2-1 About the electronic donating property

Electronic donating property in this work is investigated in terms of:

(A) Redox potential measurement, which measure the donating property in solution;

(B) Ionization potential calculation, which measure the donating property in gas.

For all the 12-S-atom TTP derivatives in Table 4, the sequence of the first redox potentials ($E_1$) is basically in consistent with the sequence of the calculated first ionization potentials ($I_1$). The $E_1$ values of **BE-TTP** and **BV-TTP** are lower than that of BE-TTF and BV-TTF, respectively. This indicates that the electron donating ability has an increase when the TTF-core in 8-S-atom TTF derivatives is replaced by the bis-fused TTF core, yielding the 12-S-atom TTP derivatives.

Table 4  Measured redox potentials and calculated ionization potentials [a], and absorption positions

| | $E_1$/V | $E_2$/V | $\Delta E_{12}$/V | $I_1$/eV | $I_2$/eV | $\Delta I/_{12}$ | $\lambda_{abs}$ [b] experimental | $\lambda_{abs}$ [c] theoretical |
|---|---|---|---|---|---|---|---|---|
| BE-TTF | 0.66 | 0.86 | 0.20 | 6.105 | 9.743 | 3.64 | 323 nm | 305.5 nm |
| **BE-TTP** | 0.58 | 0.72 | 0.14 | 5.987 | 8.887 | 2.90 | 341 nm | 333.3 nm |
| **EM-TTP** | 0.63 | 0.76 | 0.13 | 6.045 | 8.962 | 2.92 | | 334.3 nm |
| **EV-TTP** | 0.67 | 0.80 | 0.13 | 6.074 | 9.011 | 2.94 | | 333.8 nm |
| **BV-TTP** | 0.68 | 0.81 | 0.13 | 6.174 | 9.128 | 2.95 | | 332.1 nm |
| BV-TTF | 0.82 | 0.98 | 0.16 | 6.339 | 10.035 | 3.70 | | 286.5 nm |

[a]  Ionization potentials ($I_1$ and $I_2$) were calculated by DFT/b3lyp method by Gaussian-03 programs, 6-311＋g* basis set was adopted for the geometry optimizations and the energy calculations
[b]  The long-λ peak position of the UV-vis absorption spectra, recorded in toluene solvent.
[c]  The theoretical long-λ peak positions were calculated by TD-DFT/6-31(d) method.

2-2  About the π-conjugation property

π-Conjugation property can be studied by means of:

(A)  UV-vis absorption (experimentally or theoretically);

(B)  Direct structural data (X-ray structure and theoretically optimised geometric structure);

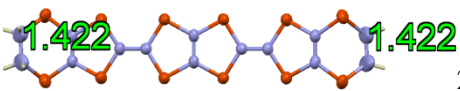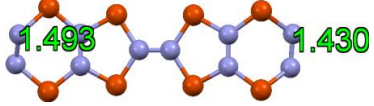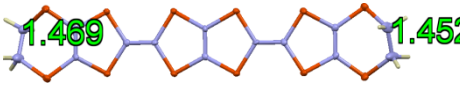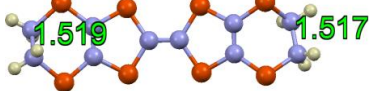(C)  $\Delta E_{12} = E_2 - E_1$ and $\Delta I = I_2 - I_1$.

(A)  The insolubility of the title TTP compounds make the record of an UV-vis absorption spectrum very difficult. The absorption of $CS_2$, the only practical solvent, severely overlaps the absorption of our compounds. Fortunately, we found that **BE-TTP** can slightly dissolve in hot toluene and had its UV-vis spectrum recorded (Fig 1b). The red-shift ($\Delta \lambda_{abs} = 341 - 323 = 18$ nm) of the absorption peaks of **BE-TTP** (relative to BE-TTF, Fig. 1b) indicates its better π-conjugation.

The calculated absorption positions (listed in the last column of Table 4) are consistant with the experimental absorption peak positions

(B)  In considering the structural data, we paid an attention to the terminal C-C bond because it is the only kind of bond that connect H atoms, which may make it possible to correlate the bond with the ^{1}HNMR data.

As we know, the X-ray measured bond lengths are temperature dependent and the DFT optimised bond lengths are basis-set dependent. As listed in Table 5, the terminal C-C bond length of **BE-TTP** is invariably shorter than that of BE-TTF, at high and low experimental temperature and at various basis-set of DFT calculation (from the moderate set of 6-311g(d) to the very large set of 6-311++(3df,3pd ). Thus, we believe that **BE-TTP** has better π-conjugation relative to BE-TTF

Table 5    The terminal C-C bond lengths of **BE-TTP** and BE-TTF

| | **BE-TTP** | | BE-TTF | |
|---|---|---|---|---|
| X-ray diffraction | 1.422 ... 1.422 (294K) | | 1.493 ... 1.430 (295K) Bull.Chem.Soc.Jpn.,1986, 59, 301. CCDC: CIMZON10 | |
| | 1.469 ... 1.452 (90K) | | 1.519 ... 1.517 (100 K) Acta cryst. C, 2002,56, 453. CCDC: CIMZON03 | |
| | Bond length/Å | Basis set | Bond length/Å | Basis set |
| Results of DFT optimization | 1.51750 | 6-311g(d) | 1.51759 | 6-311g(d) |
| | 1.51745 | 6-311+g(d) | 1.51755 | 6-311+g(d) |
| | 1.51803 | 6-311++(3df,3pd) | 1.51828 | 6-311++(3df,3pd) |

（C）As revealed in Tables 4, the $\Delta E_{12} = E_2 - E_1$ and $\Delta I_{12} = I_2 - I_1$ values monotonically decrease with increasing the π-dimension from BE-TTF to **BE-TTP**, and from BV-TTF to **BV-TTP**. Therefore the $\Delta E_{12}$ or, more conveniently, the $\Delta I$ may be a measure for degree of π-conjugation in a series of π-functional compounds.    Fig. 8 shows an example of $\Delta I$ and π-dimension correlation.
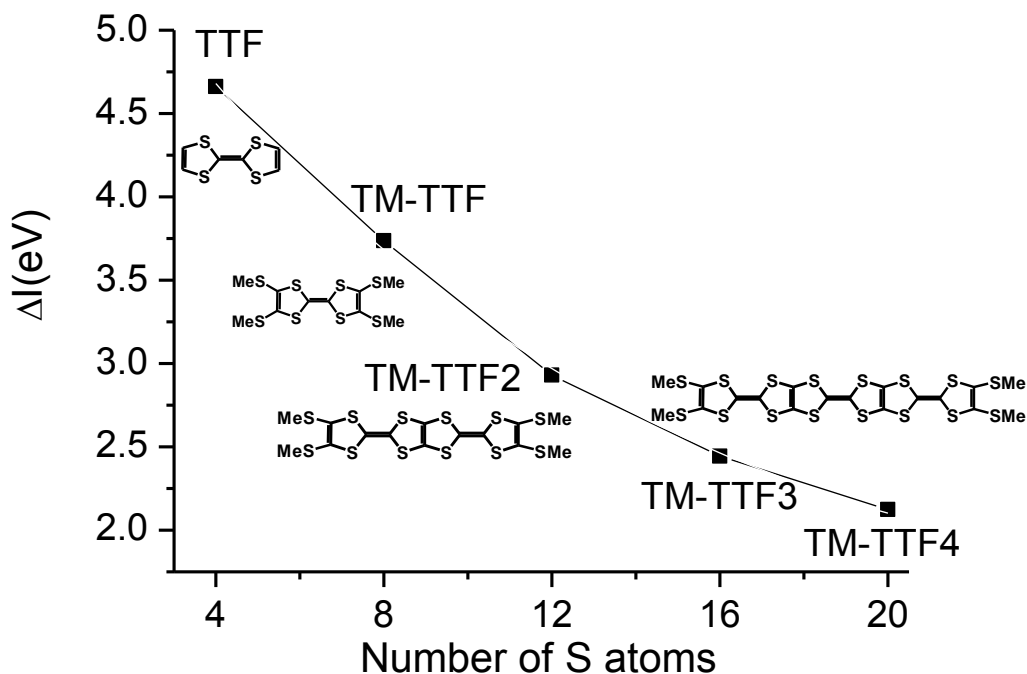


Fig. 8    The $\Delta I$ and π-dimension relation for a series of TTF derivatives. TTF2 means the bis-fused TTF core, TTF3 the tris-fused TTF core, TTF4 the tetra-fused core. The calculations were carried out by the DFT/b3lyp method by using Gaussian-03 programs. the 6-311＋g* bases were adopted for the geometry optimizations and the energy calculations for all the neutral molecules M, the radical cations $M^+$, and the dications $M^{2+}$.

**3.** The photographs of the crystal shapes of ***m*-BV-TTP**, **BE-TTP**, **EM-TTP**, and **EV-TTP** and the discussion about the determination of the conducting direction.

Generally, our crystals are long-bar-shaped or long-plate-shaped, which are well developed along a direction to form the long-axis of the crystal. The conductivity was measured along this direction of the long-axis. To know the direction of conductivity is to know the crystallographic direction [*uvw*] of this long-axis.

By using a Bruker APEX II diffractometer and the APEX program, we can determine the Miller indexes (*hkl*) of all the actual faces of the crystal. Then by using the Zone Low, the zone axis [*uvw*] can be determined which is just the direction of the long-axis of the crystal.
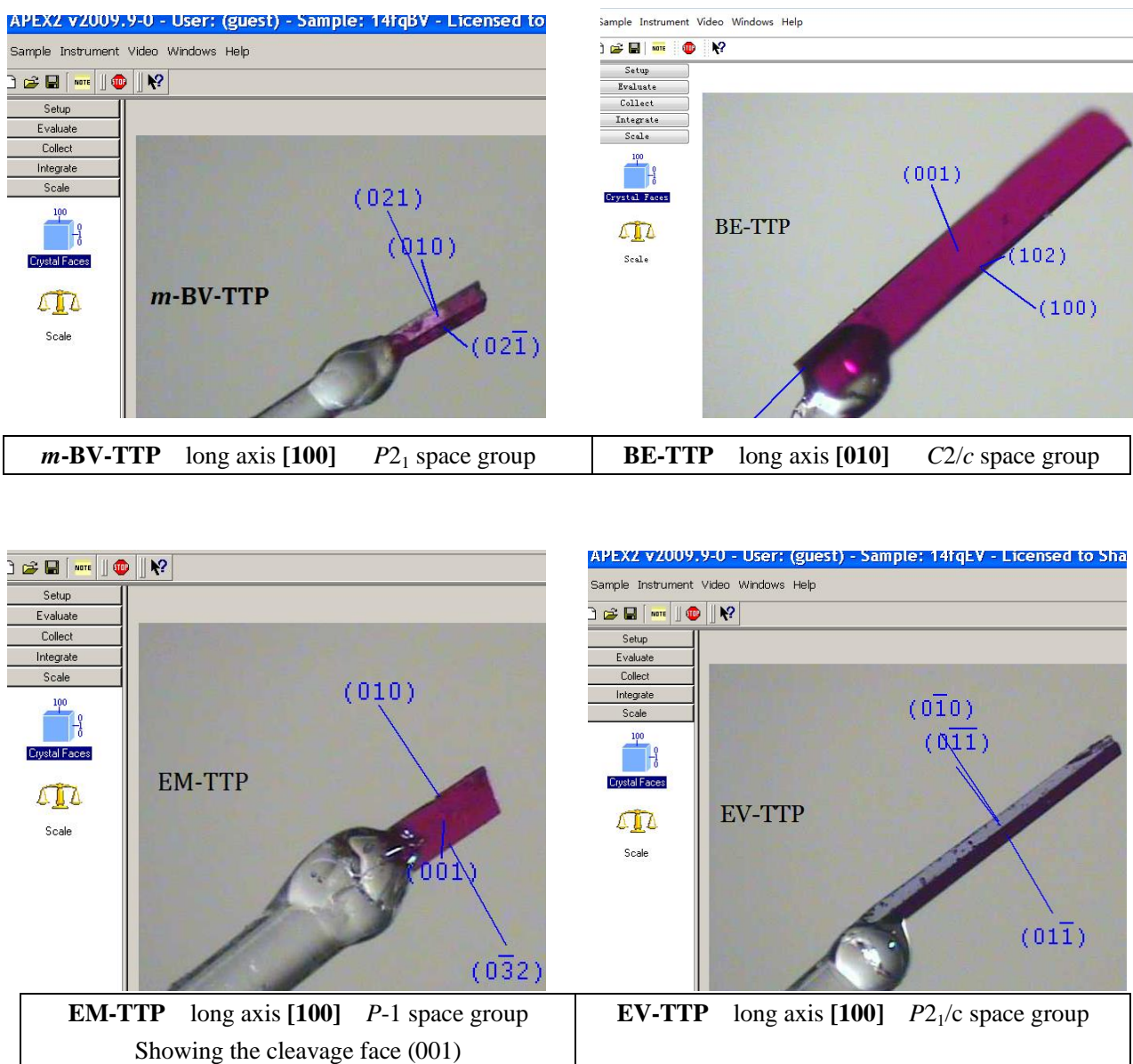


| ***m*-BV-TTP**    long axis **[100]**    $P2_1$ space group | **BE-TTP**    long axis **[010]**    $C2/c$ space group |
|---|---|



| **EM-TTP**    long axis **[100]**    $P$-1 space group<br>Showing the cleavage face (001) | **EV-TTP**    long axis **[100]**    $P2_1/c$ space group |
|---|---|

**Fig. 9** The photographs of the crystal shapes of ***m*-BV-TTP, BE-TTP**, **EM-TTP**, and **EV-TTP**.

**4.** A structure drawing of TTM-TTP and TTC$_4$-TTP (based on the CCDC X-ray data) with the electronic transfer integral (*t*) being indicated.
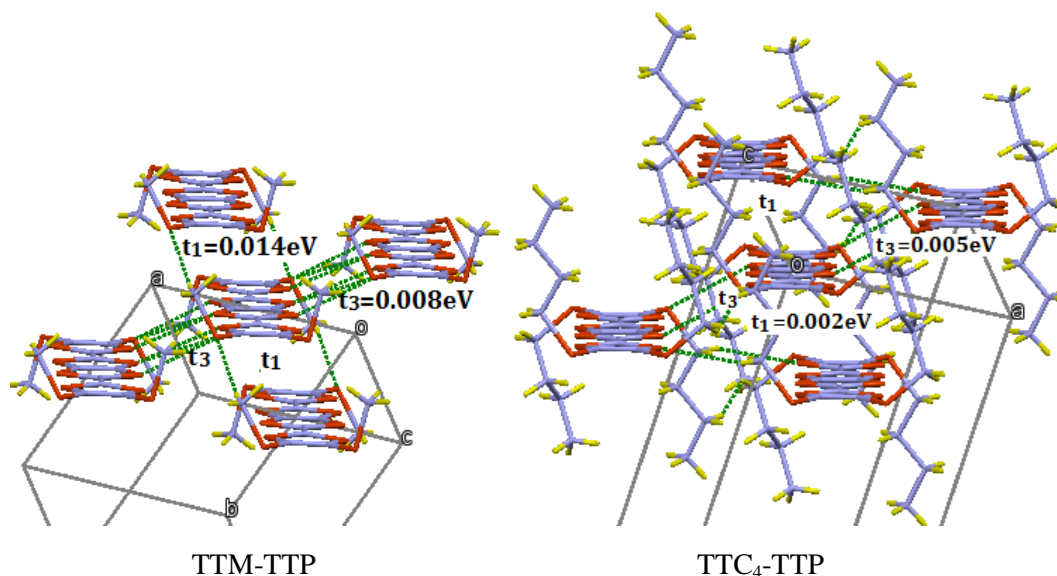


TTM-TTP                    TTC$_4$-TTP

**Fig. 10** A structure drawing of TTM-TTP (CCDC No. YATYEX ) and TTC$_4$-TTP (CCDC No. MEZWUJ) with the electronic transfer integral (*t*) being indicated.    The long terminal alkyl groups make the molecules shift to each other along the short molecular axis and therefore depart from normal face-to-face overlap. which will greatly reduce the columnar π-π interactions.

**5.** A photograph of a **EV-TTP** crystal with two gold wires and gold-paste on it for conductivity measurement.
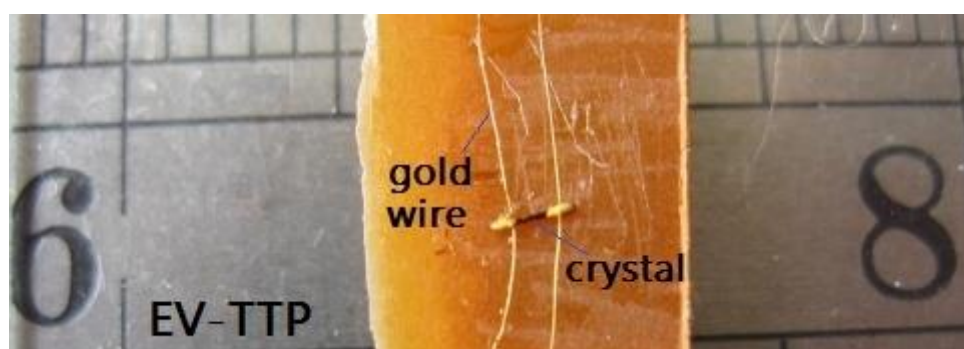


**Fig. 11** A photograph of a **EV-TTP** crystal for conductivity measurement. Two gold wires, 0.03 mm in diameter and 1.2 mm apart from each other, were run perpendicularly across the long-bar crystal of **EV-TTP** with dimensions of 1.8 × 0.08× 0.04 mm and fixed in place using gold-paste.

**6.**    DTA and TG curves of *m*-**BV-TTP**, **EV-TT**P, **BE-TTP**, and **EM-TTP**



*m*-**BV-TTP**



**EV-TTP**



**BE-TTP**
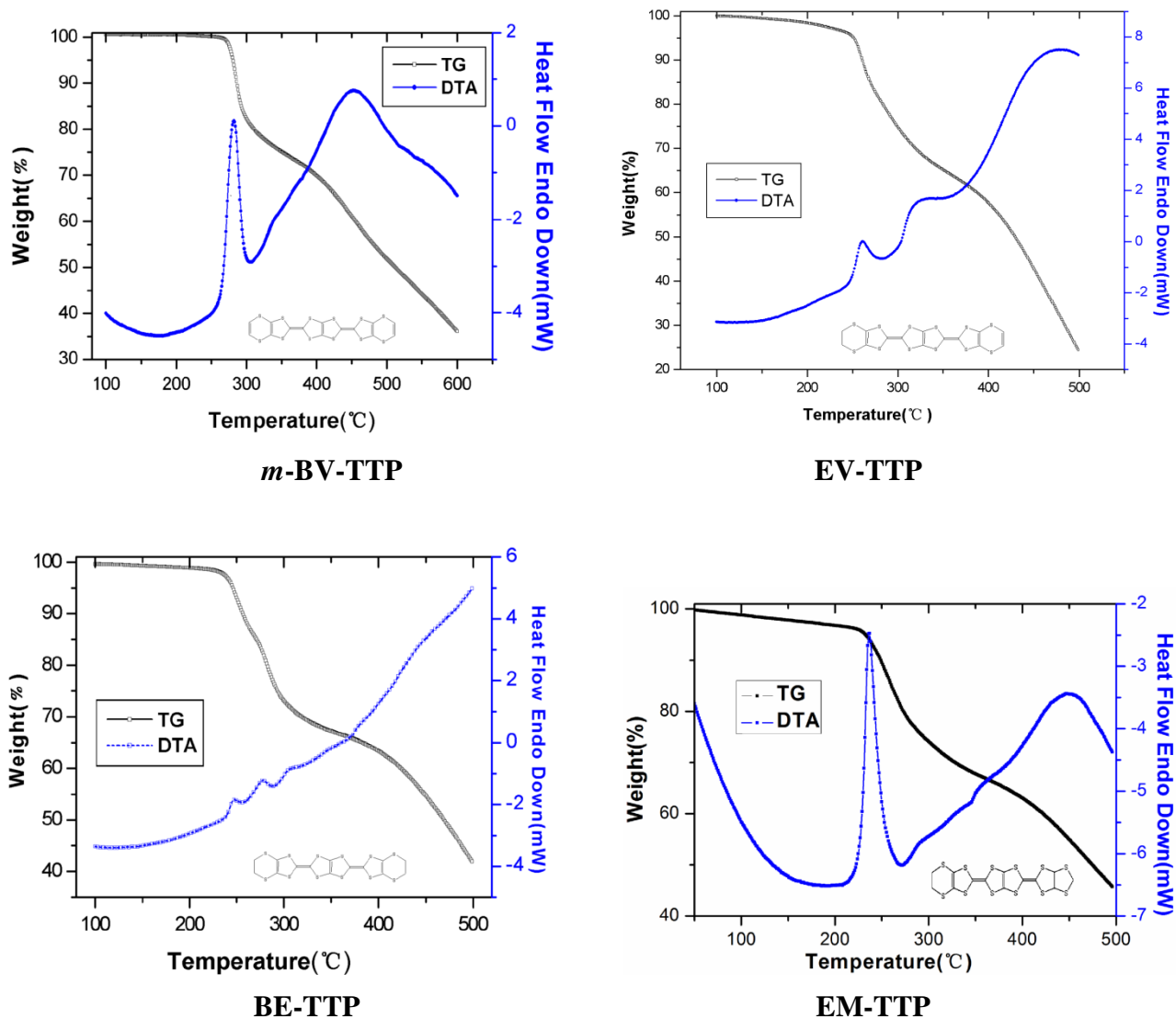


**EM-TTP**

**Fig. 12**    DTA and TG curves of *m*-**BV-TTP, EV-TTP, BE-TTP**, and **EM-TTP**

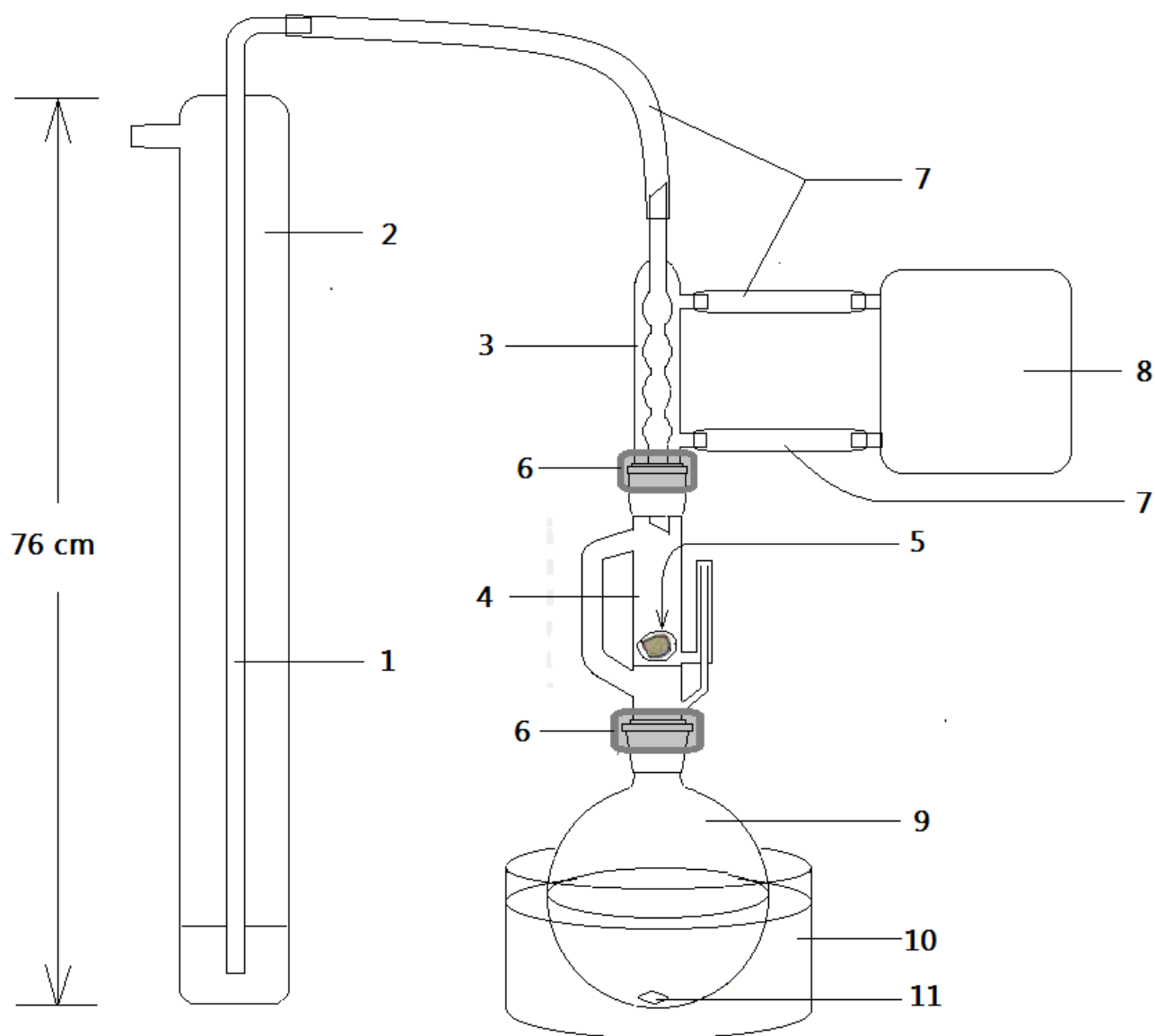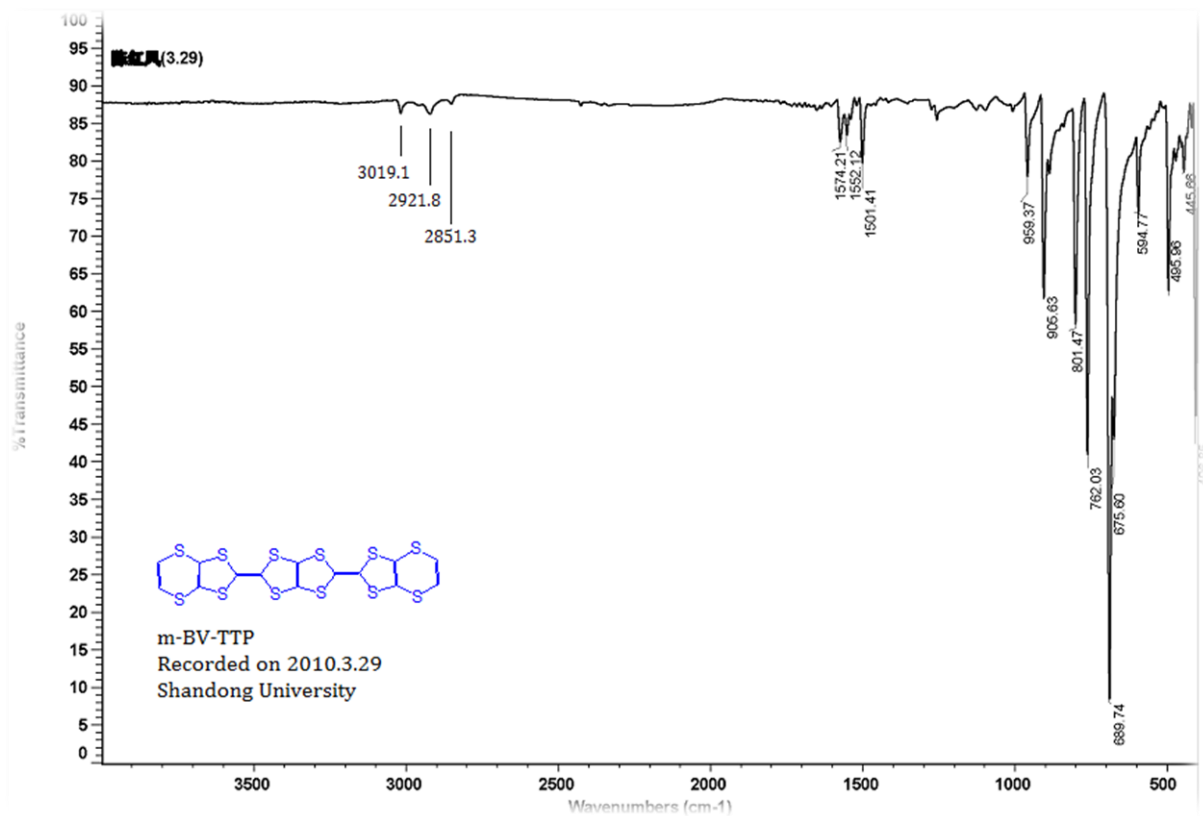**7.** A drawing of the improved Soxhlet's extractor.
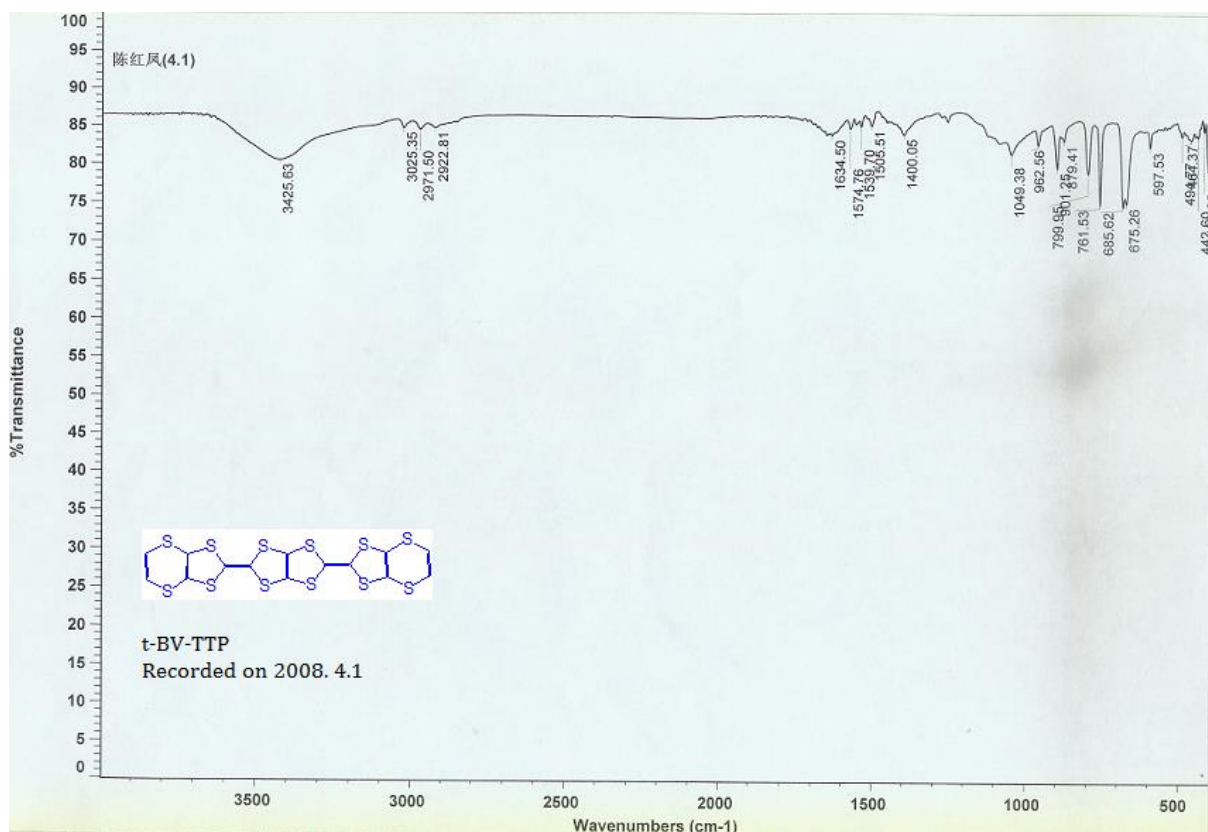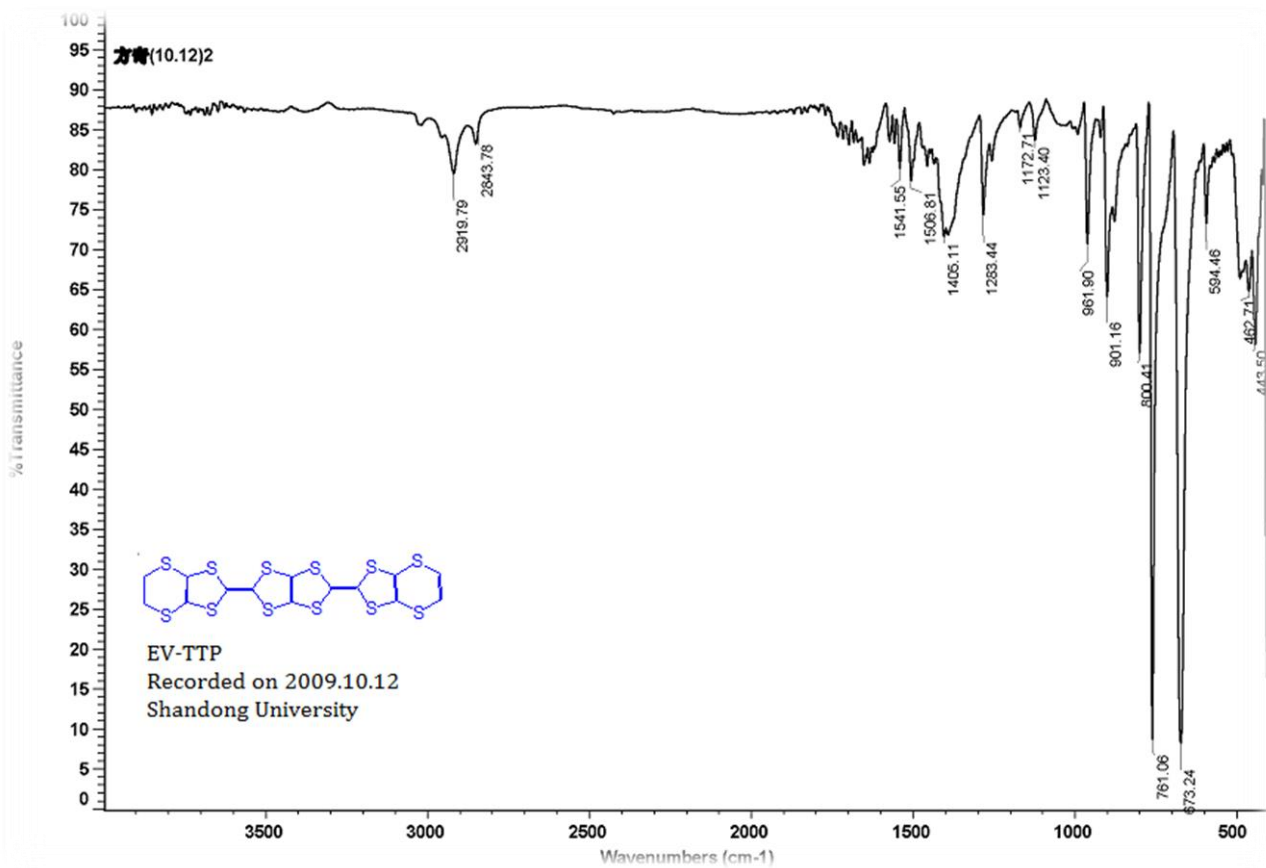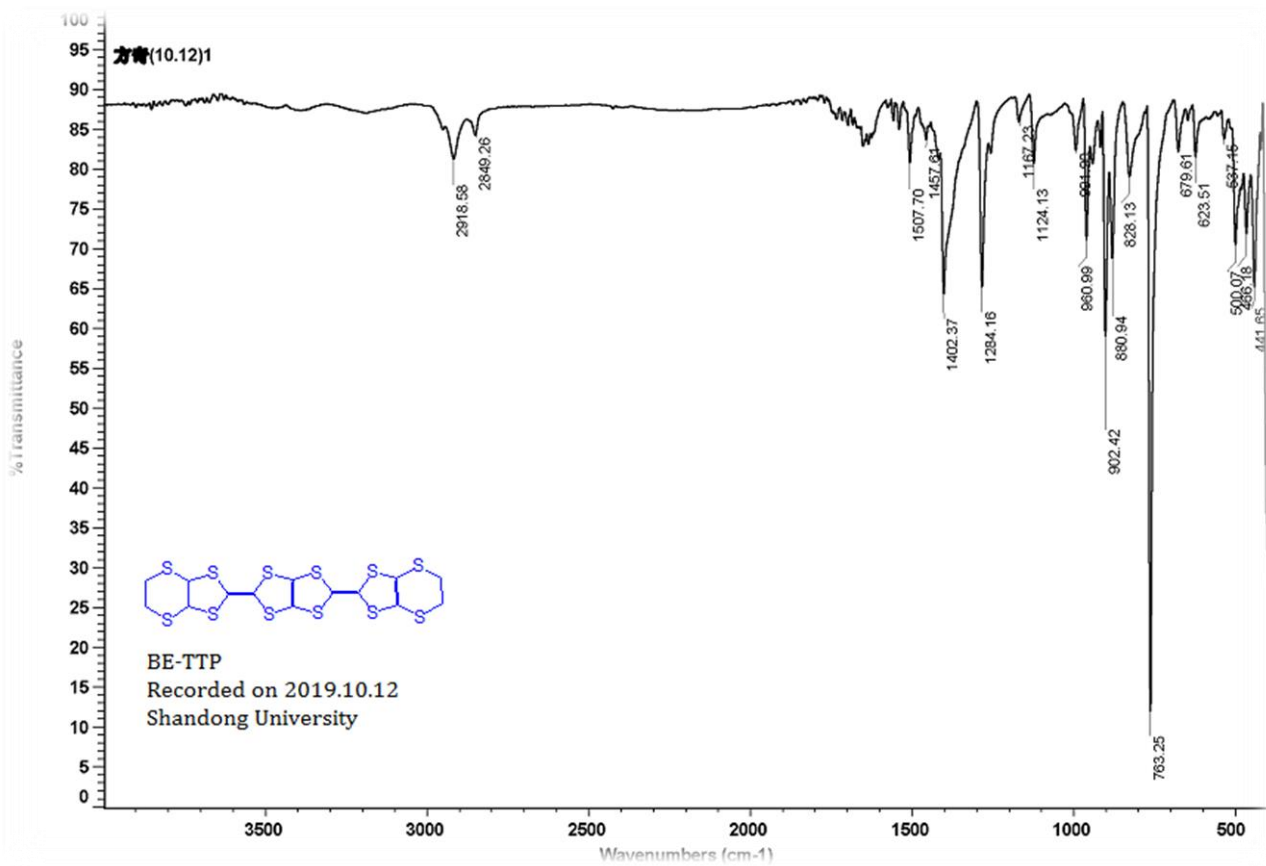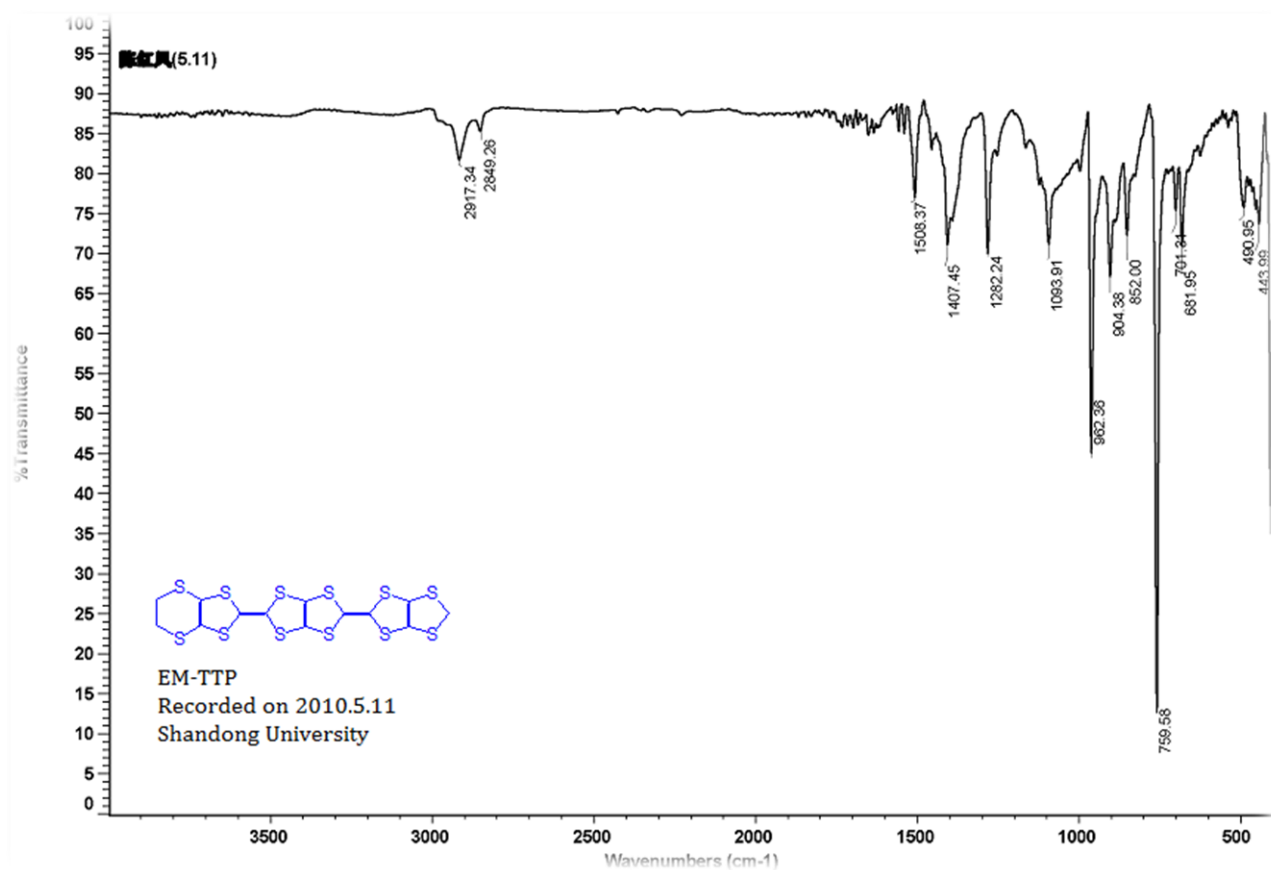


**Fig. 13**   A improved Soxhlet's extractor.

1 and 2: Mercury bubbler; 3: Condensor; 4: Chamber for solid sample; 5: Solid sample in filter paper; 6: Parafilm; 7: Silicone soft tube; 8: Low-temperature cooling liquid circulating pump; 9: Flask; 10: Silicone oil heating bath; 11: Stirrer.   The more details can be found in a PRC Patent of the same authors.

**8.** IR spectra of *t*-**BV-TTP**, *m*-**BV-TTP**, **BE-TTP**, **EV-TTP**, and **EM-TTP**

BE-TTP
Recorded on 2019.10.12
Shandong University



EV-TTP
Recorded on 2009.10.12
Shandong University

IR spectra of **EV-TTP**



IR spectra of **EM-TTP**

**Fig. 14** IR spectra of ***t*-BV-TTP**, ***m*-BV-TTP, BE-TTP, EV-TTP** and **EM-TTP**

The triclinic ***t*-BV-TTP** and monoclinic ***m*-BV-TTP** can be identified by checking a CH peak, which is at 2972 cm$^{-1}$ for ***t*-BV-TTP** and 2922 cm$^{-1}$ for ***m*-BV-TTP**.   The IR spectrum of **EV-TTP** is similar to the spectral overlap of **BE-TTP** and ***m*-BV-TTP**. Its 1283m and 673s sharp peaks, for example, are corresponding to the character peaks of **BE-TTP** (1284s) and ***m*-BV-TTP** (676s), respectively.