

## Supplementary information

**Synthesis and characterization of *N,N'*-bis(2-thienylmethylene)-1,X-diaminobenzene isomers (X = 2, 3, 4) and their metal complexes**

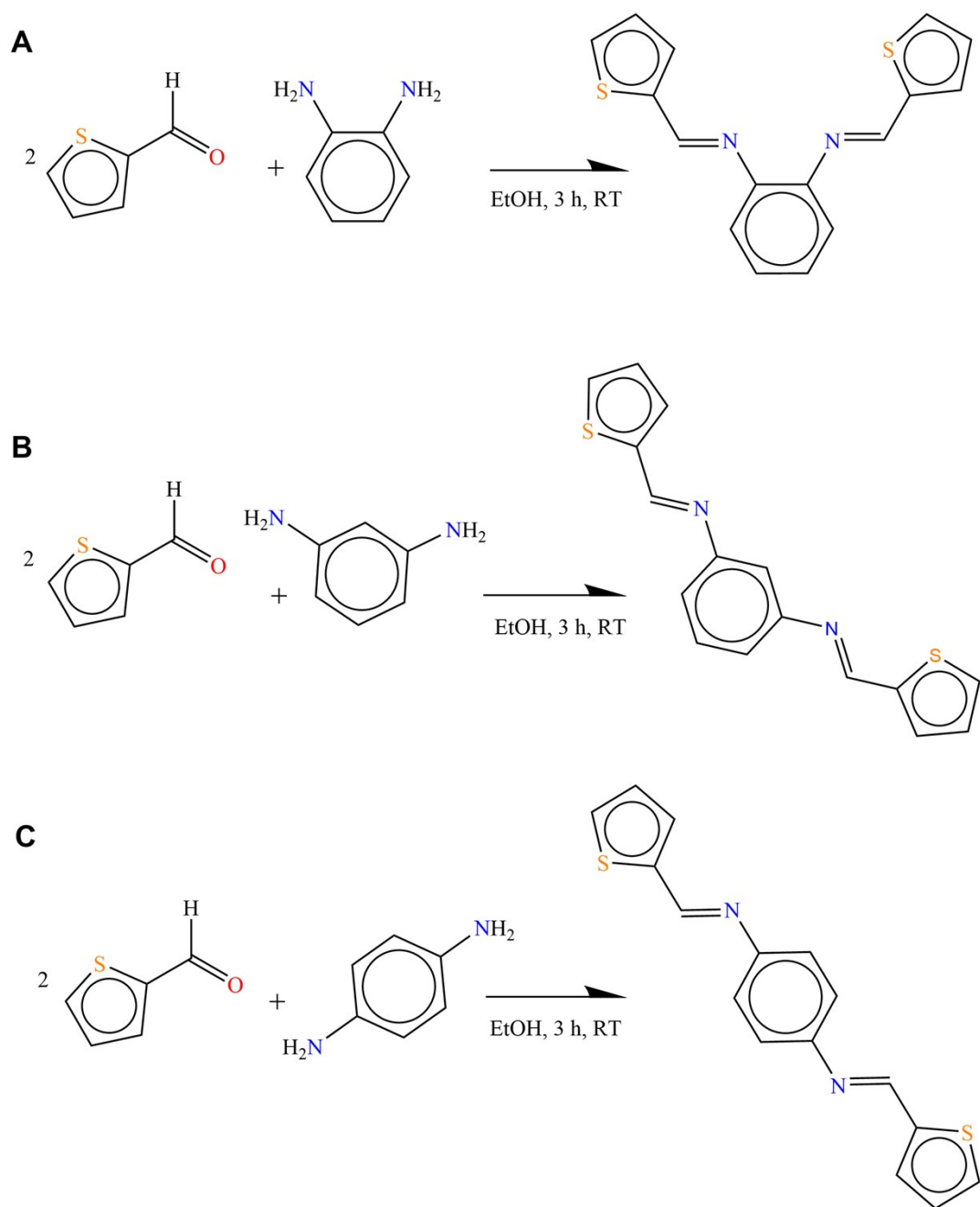
**Parastoo Vahdatiyekta<sup>a</sup>, Mohammed Zniber<sup>a</sup>, Kostiantyn Nikiforow<sup>b</sup>, Tan-Phat Huynh<sup>a\*</sup>**

<sup>a</sup>Laboratory of Molecular Science and Engineering, Åbo Akademi University, 20500 Turku,  
Finland

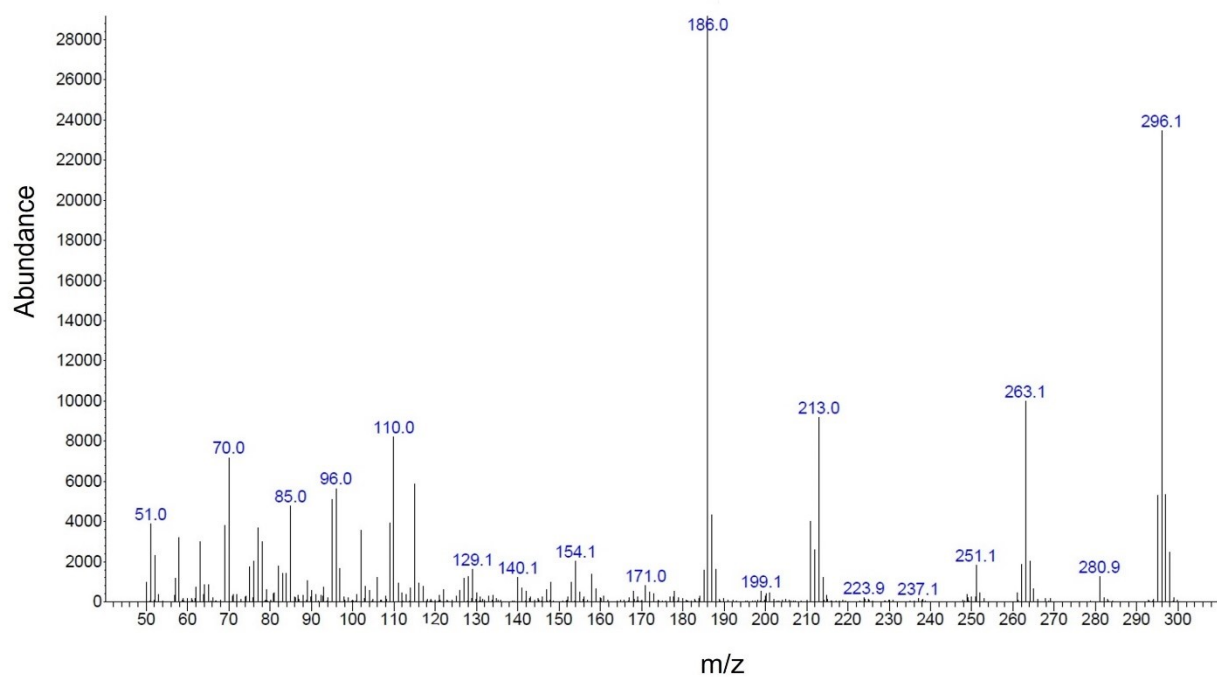
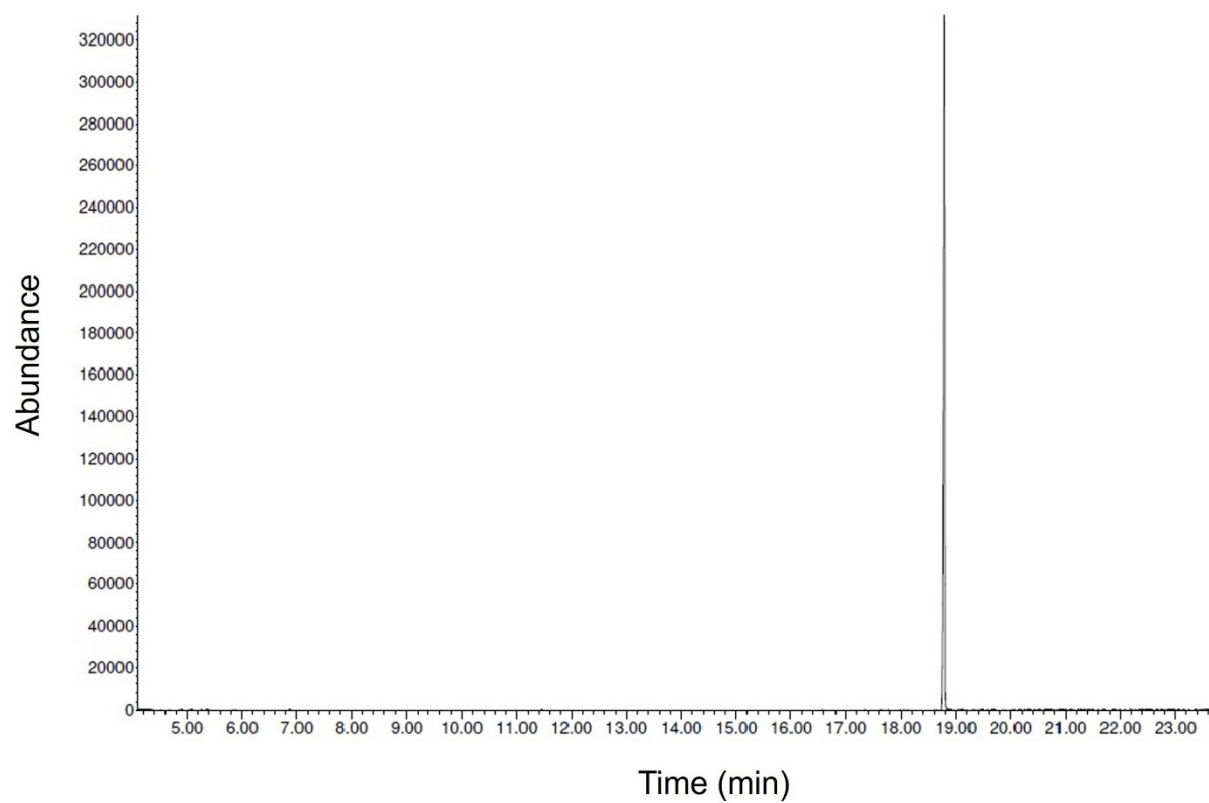
<sup>b</sup>Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Poland

\*Corresponding author. Tel.: +358 504337295

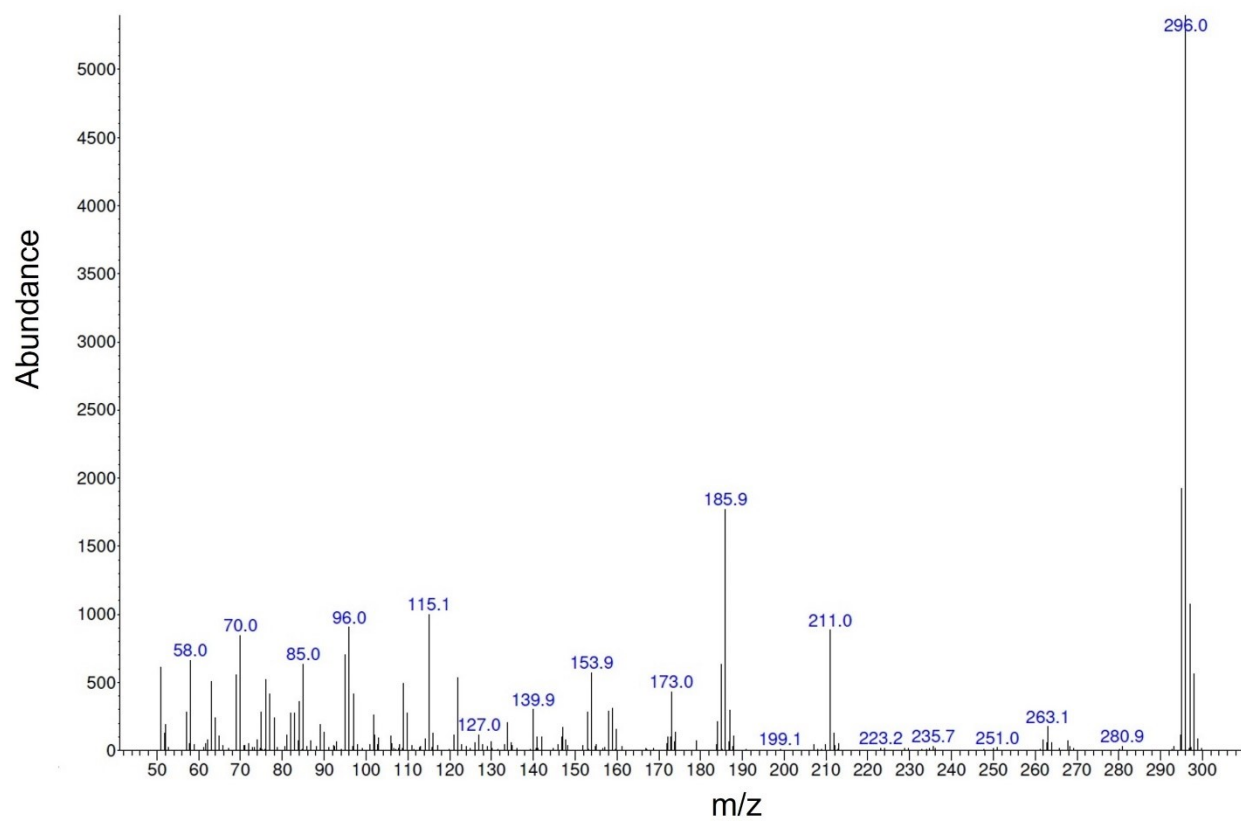
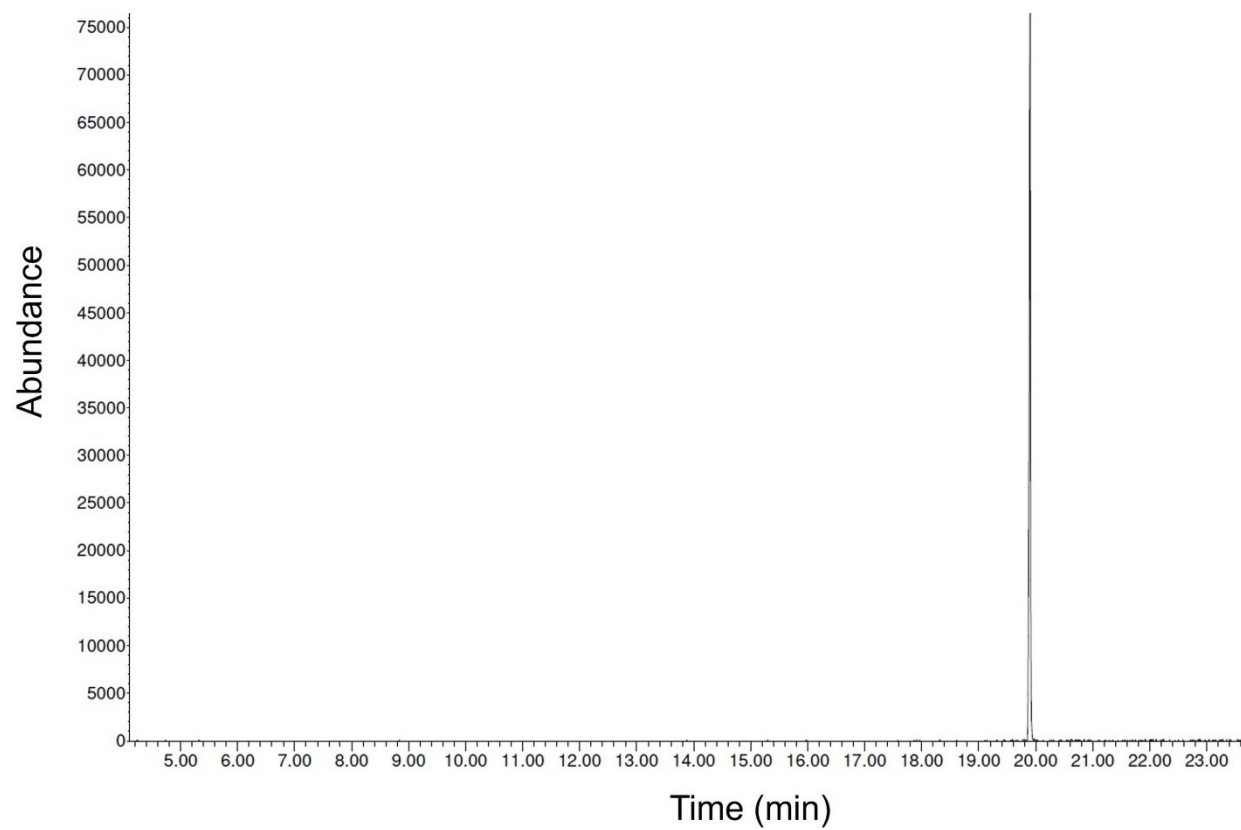
Email: [tan.huynh@abo.fi](mailto:tan.huynh@abo.fi)



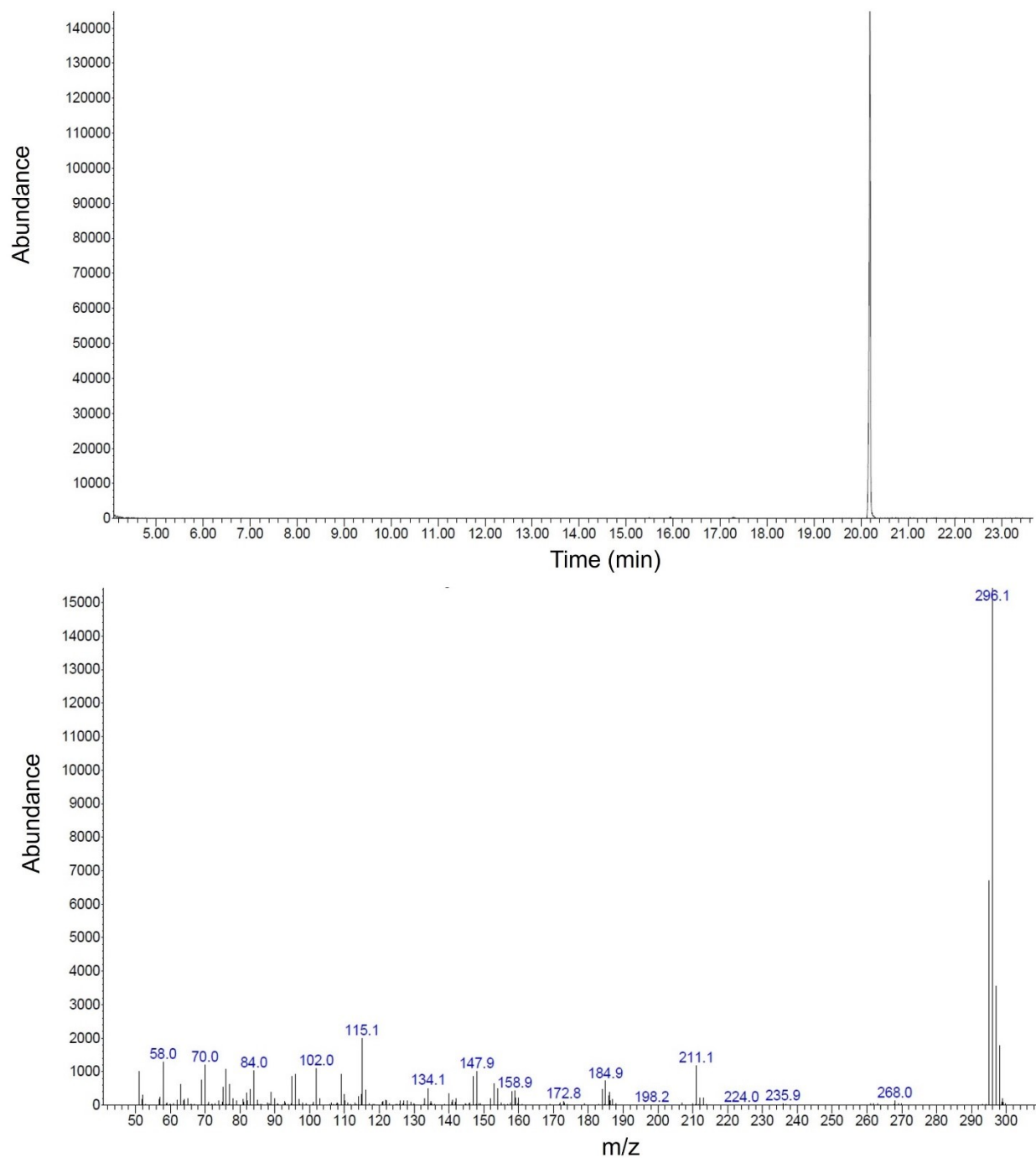
**Fig. S1** The route for the synthesis of A) o-BTMD, B) m-BTMD, and C) p-BTMD.



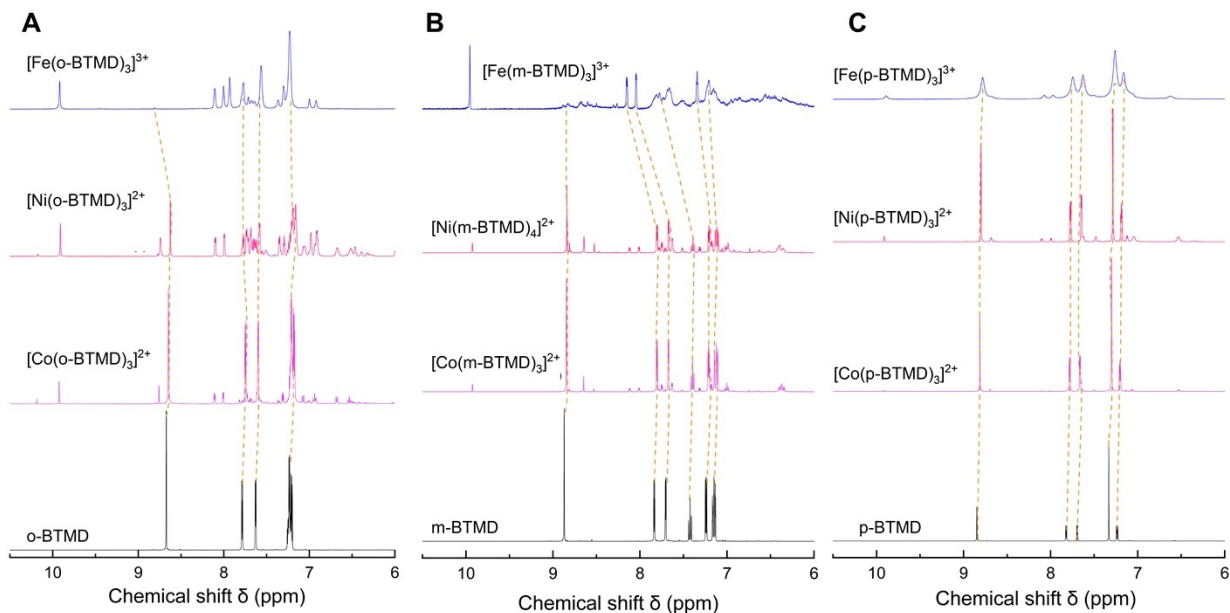
**Fig. S2** Mass spectrum of *o*-BTMD



**Fig. S3** Mass spectrum of *m*-BTMD



**Fig. S4** Mass spectrum of *p*-BTMD



**Fig. S5**  $^1\text{H}$ NMR spectra of A) *o*-BTMD, B) *m*-BTMD, and C) *p*-BTMD complexes with; Co(II)chloride hexahydrate, Fe(III)chloride hexahydrate, and Ni(II)nitrate hexahydrate in DMSO- $\text{d}_6$ .

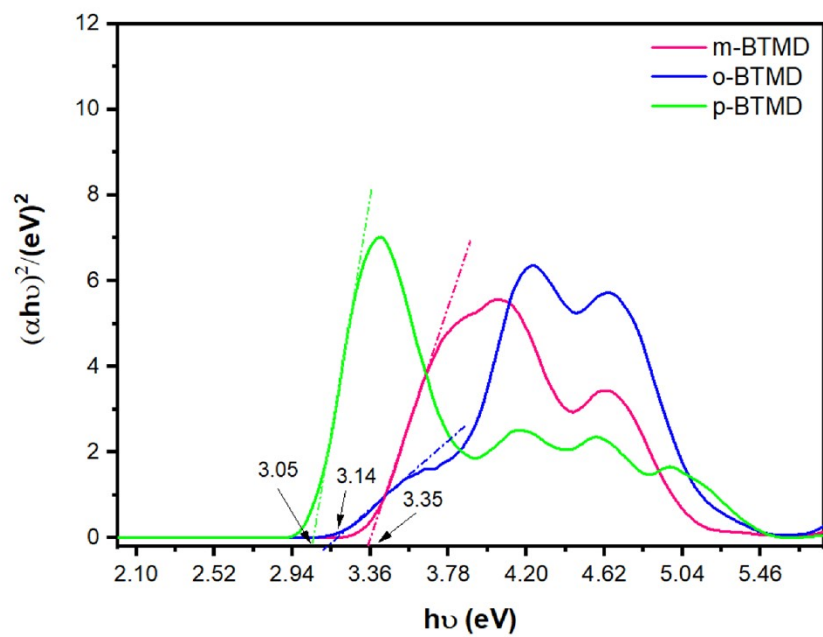
Eq. S1

$$(ah\nu)^n = B (h\nu - E_g)$$

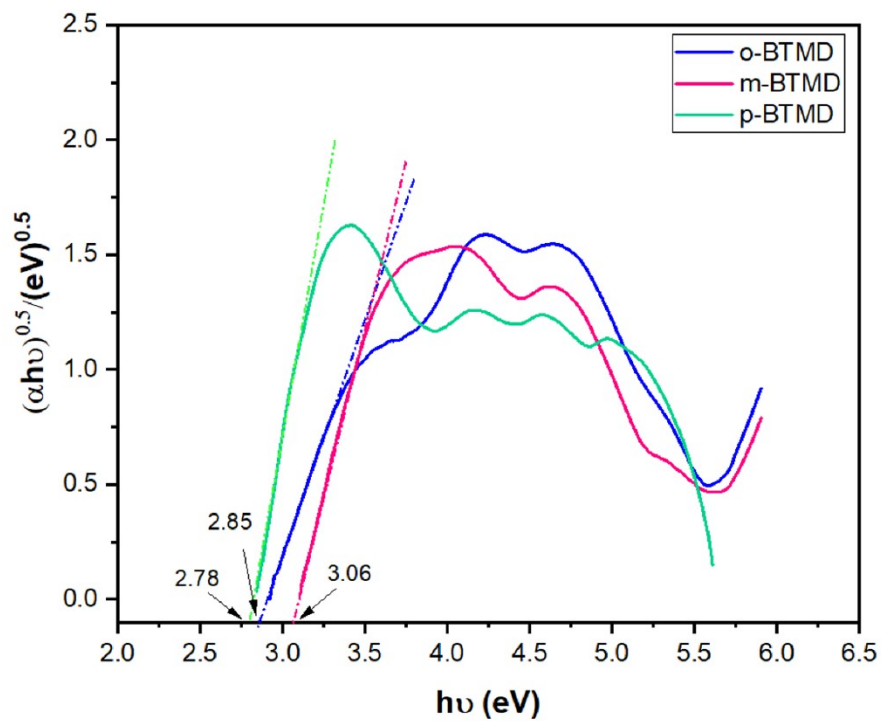
Eq. S2

$$\alpha = \frac{2.303A}{l}$$

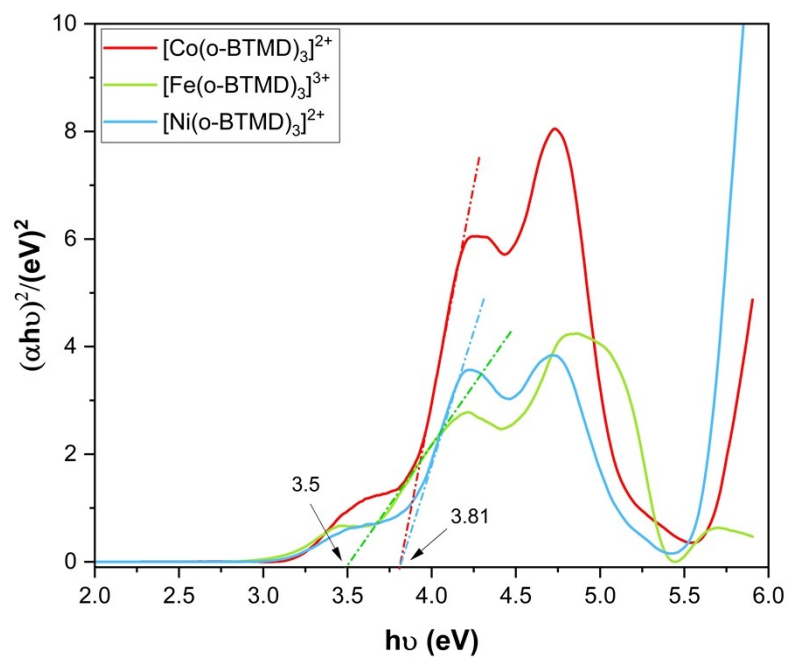
In Eq. S1  $h\nu$  corresponds to the photon energy,  $B$  is the bandgap tailing parameter, which is considered 1 in general,  $\alpha$  is the absorption coefficient, which is calculated by Eq. S2, where  $A$  is the absorbance and  $l$  is the path length.  $n$  denotes the nature of electronic transition which has the value 0.5 and 2 for indirect and direct transition, respectively.



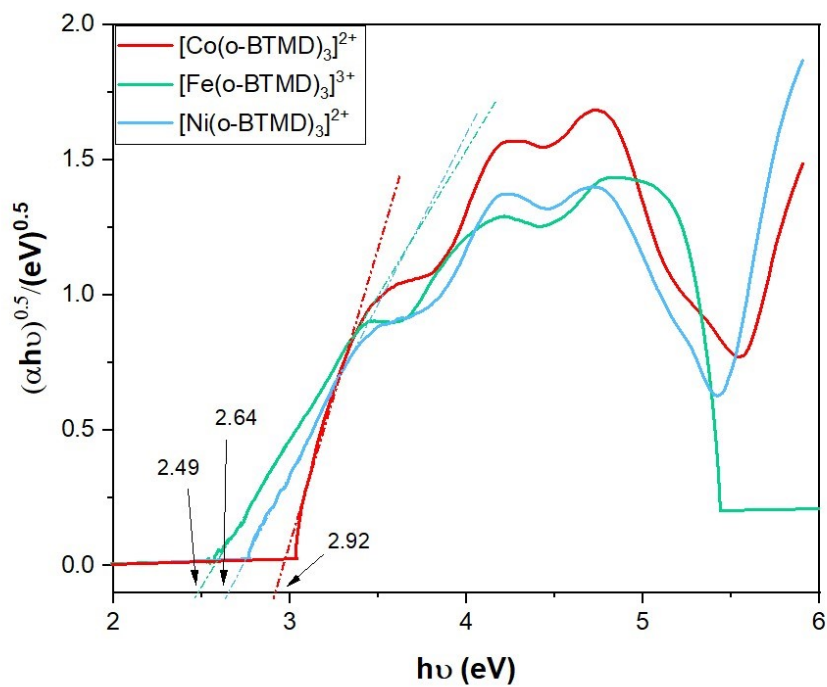
**Fig. S6** The plots of  $(\alpha h\nu)^2$  versus  $h\nu$  for determination of the direct bandgap of isomers in acetonitrile.



**Fig. S7** The plots of  $(\alpha h\nu)^{0.5}$  versus  $h\nu$  for determination of the indirect bandgap of isomers in acetonitrile.

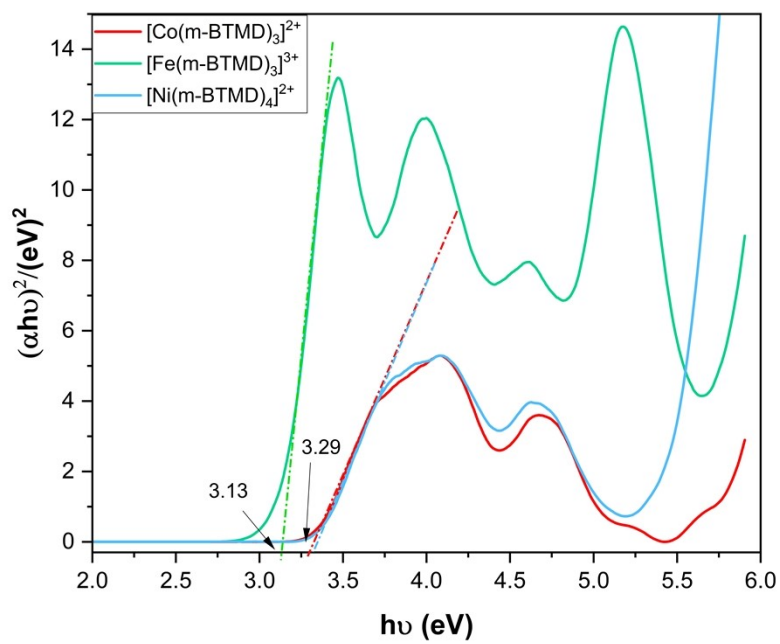


**Fig. S8** The plots of  $(\alpha h\nu)^2$  versus  $h\nu$  for determination of the direct bandgap of *o*-BTMD complexes in acetonitrile.

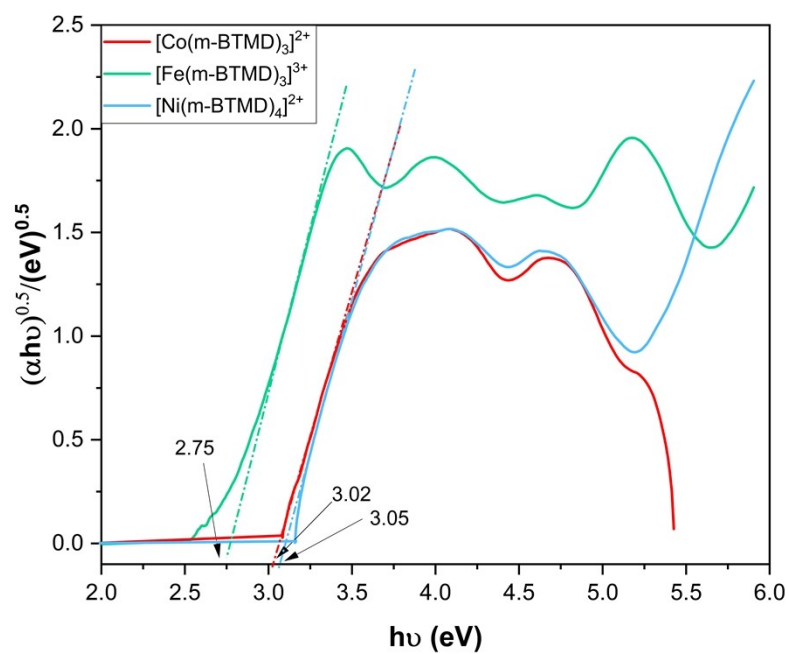


**Fig. S9** The plots of  $(\alpha h\nu)^{0.5}$  versus  $h\nu$  for determination of the indirect bandgap of *o*-BTMD complexes in acetonitrile.

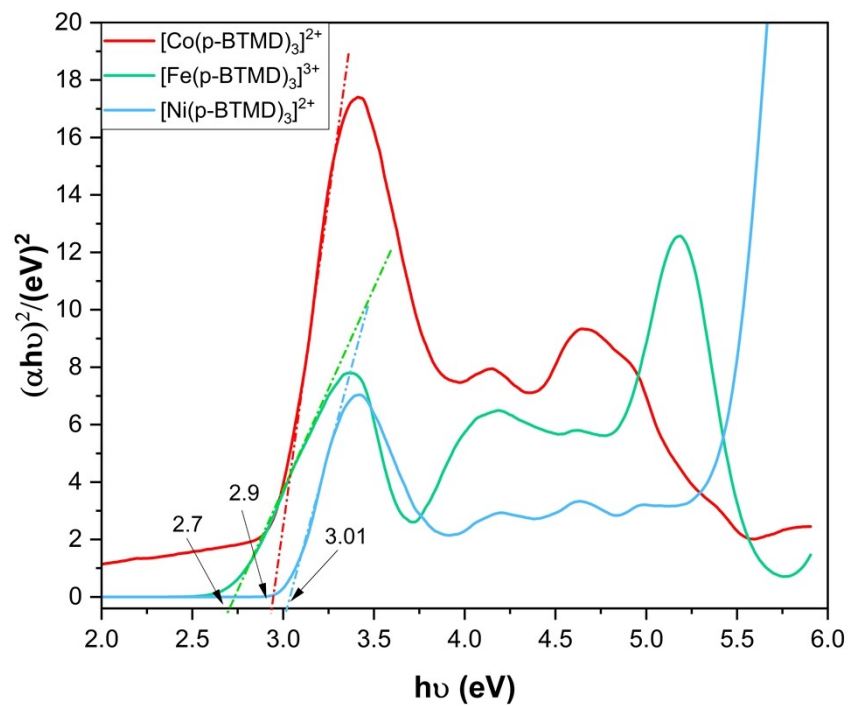




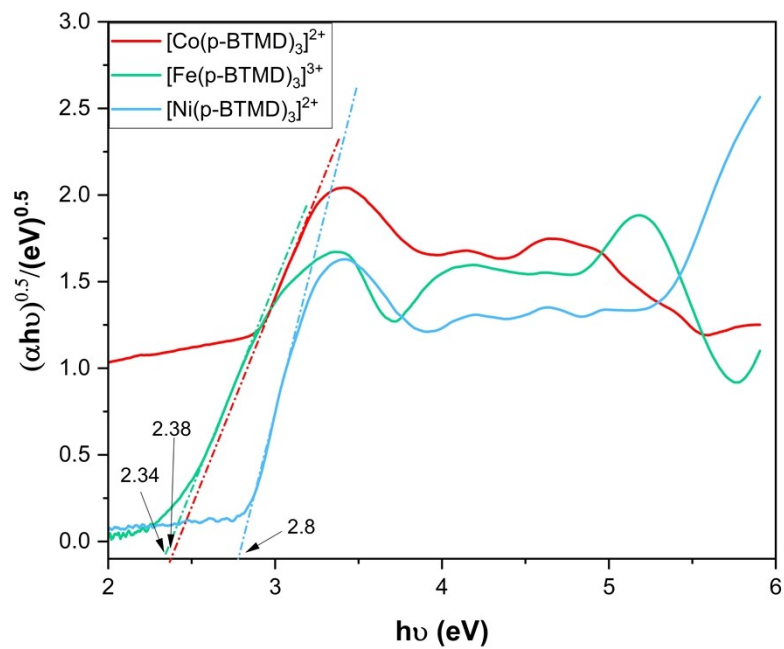
**Fig. S10** The plots of  $(\alpha h\nu)^2$  versus  $h\nu$  for determination of the direct bandgap of *m*-BTMD complexes in acetonitrile.



**Fig. S11** The plots of  $(\alpha h\nu)^{0.5}$  versus  $h\nu$  for determination of the indirect bandgap of *m*-BTMD complexes in acetonitrile.



**Fig. S12** The plots of  $(\alpha h\nu)^2$  versus  $h\nu$  for determination of the direct bandgap of *p*-BTMD complexes in acetonitrile.

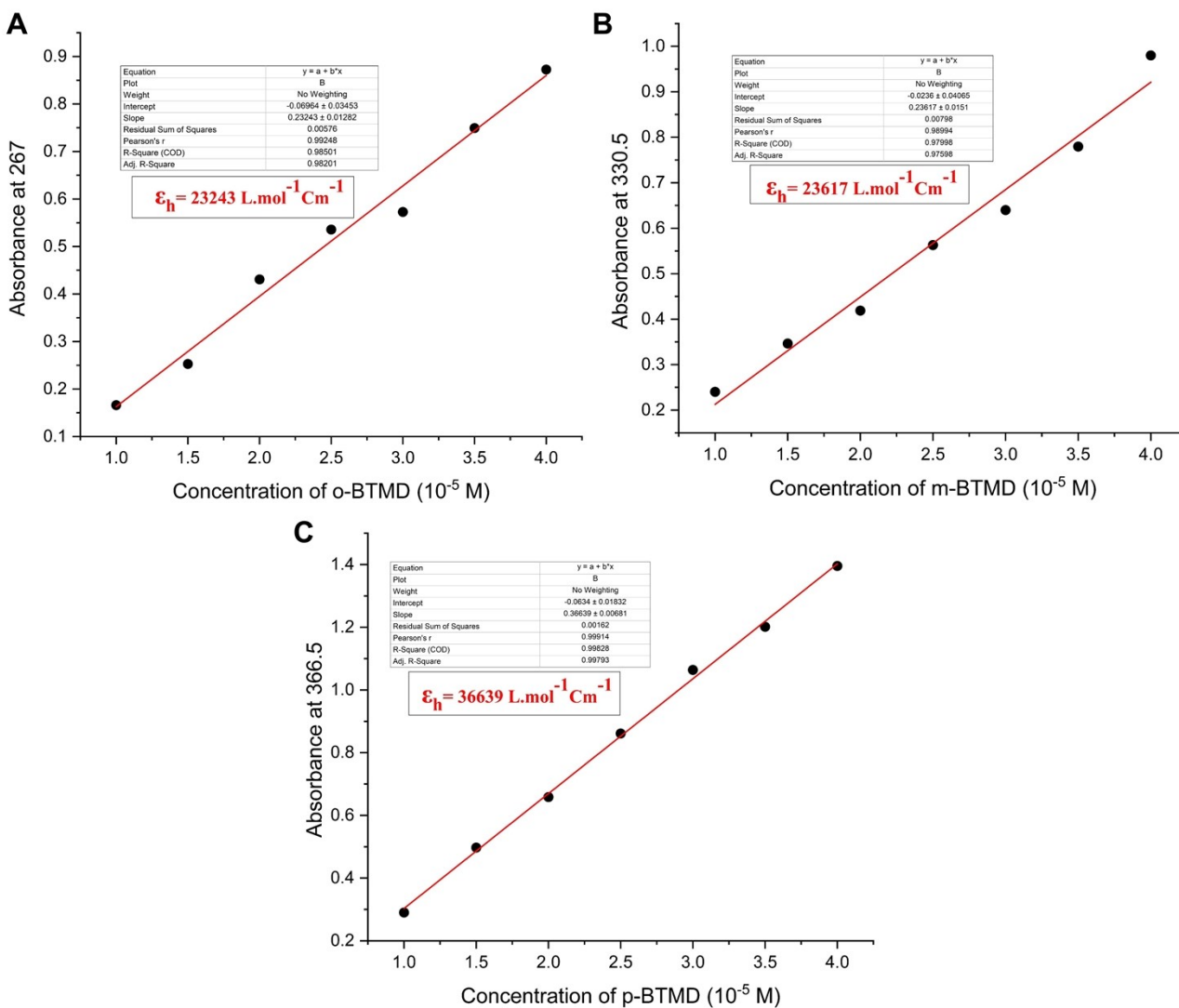


**Fig. S13** The plots of  $(ah\nu)^{0.5}$  versus  $h\nu$  for determination of the indirect bandgap of *p*-BTMD complexes in acetonitrile.

It's worth to mention that in the case of meta, the ring bend is clearly present which is absent in ortho and para, that's why there are two or sometimes three peaks in the range of 680 to 900  $\text{cm}^{-1}$ .

**Table S1.** FTIR and RAMAN Information of Isomers.

Isomer	FTIR ( $\text{cm}^{-1}$ )	Raman ( $\text{cm}^{-1}$ )
<i>o</i> -BTMD	<ul style="list-style-type: none"> <li>2000-1700 (very weak) (overtones)</li> <li>3107, 3066, 2871 (weak) (=C-H aromatic stretch)</li> <li>818, 701 (strong) (=C-H aromatic bending)</li> <li>1618, 1582, 1560, 1474, 1424 (medium) (Aromatic C=C stretch)</li> <li>1604 (medium) (C=N stretch)</li> <li>1186, 1043 (medium) (C-S aromatic stretch)</li> <li>450-570 (medium) (C-S aromatic bending)</li> </ul>	<ul style="list-style-type: none"> <li>3099, 3079 (weak) (=C-H aromatic stretch)</li> <li>950, 640 (weak) (=C-H aromatic bending)</li> <li>1620, 1584, 1560, 1426 (strong) (Aromatic C=C stretch)</li> <li>1607 (medium) (C=N stretch)</li> <li>1194, 1155 (medium) (C-S aromatic stretch)</li> </ul>
<i>m</i> -BTMD	<ul style="list-style-type: none"> <li>2000-1690 (very weak) (overtones)</li> <li>3099, 3080, 2871 (weak) (=C-H aromatic stretch)</li> <li>791, 855 (medium) (=C-H aromatic bending)</li> <li>1569, 1478, 1424 (medium to strong) (Aromatic C=C stretch)</li> <li>705, 687 (very strong) (Aromatic C=C bending)</li> <li>1604 (medium) (C=N stretch)</li> <li>1042, 1144 (medium) (C-S aromatic stretch)</li> <li>450-570 (medium) (C-S aromatic bending)</li> </ul>	<ul style="list-style-type: none"> <li>3100, 3080 (weak) (=C-H aromatic stretch)</li> <li>957, 650 (weak) (=C-H aromatic bending)</li> <li>1574, 1427, 1372, 1322 (medium to strong) (Aromatic C=C stretch)</li> <li>1609 (strong) (C=N stretch)</li> <li>1204 (medium) (C-S aromatic stretch)</li> </ul>
<i>p</i> -BTMD	<ul style="list-style-type: none"> <li>2000-1670 (very weak) (overtones)</li> <li>3066, 2871 (weak) (=C-H aromatic stretch)</li> <li>849, 807, 723 (medium to strong) (=C-H aromatic bending)</li> <li>1493, 1478, 1423 (weak to medium) (Aromatic C=C stretch)</li> <li>1605 (medium) (C=N stretch)</li> <li>1043, 1196 (medium) (C-S aromatic stretch)</li> <li>450-570 (medium) (C-S aromatic bending)</li> </ul>	<ul style="list-style-type: none"> <li>3100, 3060 (weak) (=C-H aromatic stretch)</li> <li>966, 811 (weak) (=C-H aromatic bending)</li> <li>1585, 1427 (medium to very strong) (Aromatic C=C stretch)</li> <li>1615 (medium) (C=N stretch)</li> <li>1195, 1162 (medium) (C-S aromatic stretch)</li> </ul>



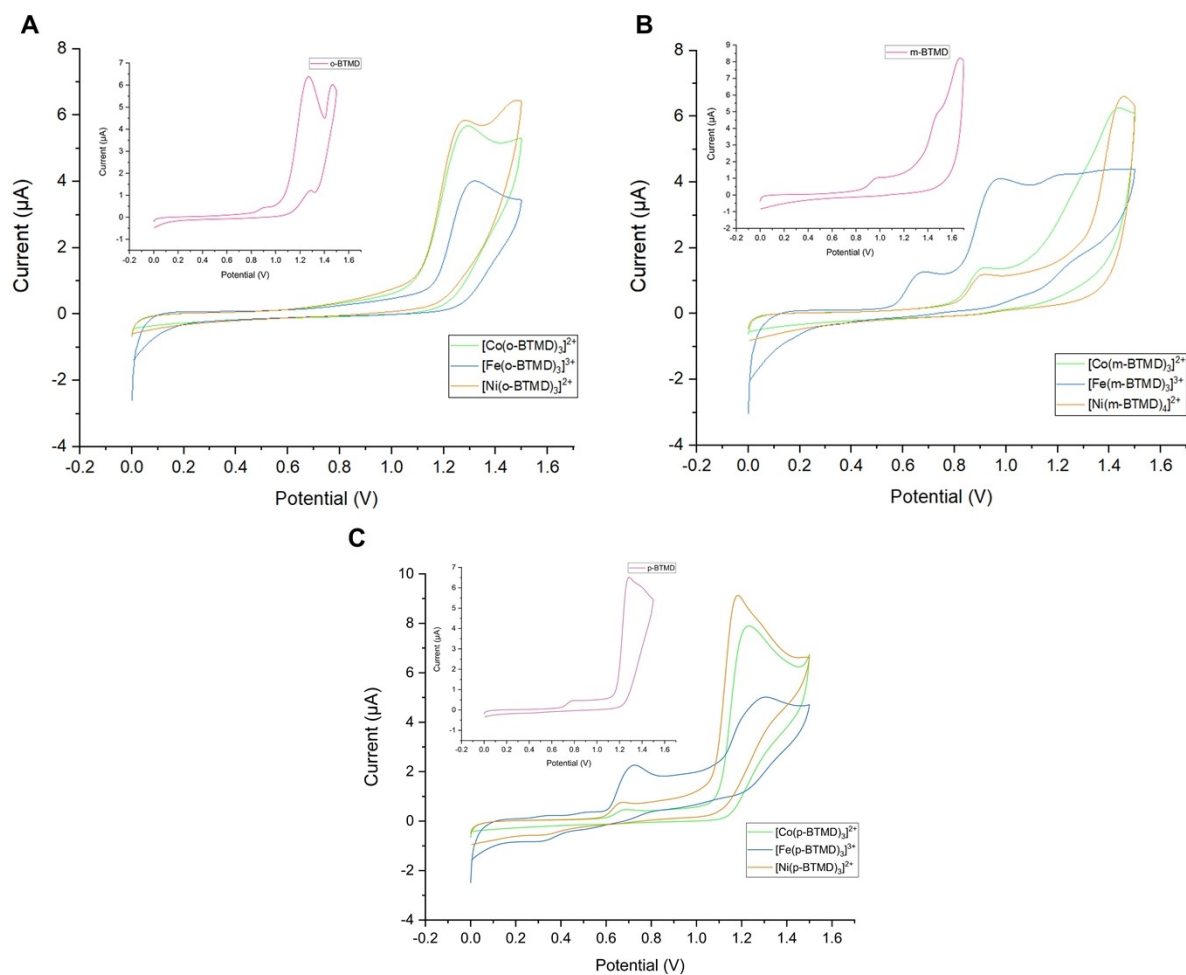
**Fig. S14** Beer-Lambert plots for; A) *o*-BTMD, B) *m*-BTMD, C) *p*-BTMD

**Table S2.** Complexation Information of BTMDs with Transition Metal Ions.

Ligand/Metal ion	Stoichiometric Ratio [ligand]:[M]	Complex Concentration (M)	Binding Constant ( $\text{M}^{-1}$ )
<i>o</i> -BTMD/ Co(II)	3:1	4.8144e-07 (Abs value)	3.4735e+03
<i>o</i> -BTMD/ Fe(III)	3:1	2.4462e-06	5.6957e+08

<i>o</i> -BTMD/ Ni(II)	3:1	8.2362e-07	8.0591e+03
<i>m</i> -BTMD/ Co(II)*	—	—	—
<i>m</i> -BTMD/ Fe(III)	3:1	6.1862e-07 (Abs value)	5.0177e+03
<i>m</i> -BTMD/ Ni(II)	4:1	1.0766e-07	6.2809e+07
<i>p</i> -BTMD/ Co(II)	3:1	1.1044e-06	1.4389e+04
<i>p</i> -BTMD/ Fe(III)	3:1	2.5829e-07	1.5600e+03
<i>p</i> -BTMD/ Ni(II)	3:1	1.8231e-06	6.2276e+04

\**m*-BTMD's UV-Vis spectrum didn't show any changes in absorbance by adding Co(II). Even in high ratio of 1: 0.8 *m*-BTMD: Co(II).



**Fig. S15** Cyclic voltammetry graphs of A) *o*-BTMD, B) *m*-BTMD, and C) *p*-BTMD complexes with; Co(II)chloride hexahydrate, Fe(III)chloride hexahydrate, and Ni(II)nitrate hexahydrate. Scan rate: 5 mVs<sup>-1</sup>.