

**Supporting Information**  
**Metal-Promoted Intermolecular Electron Transfer in**  
**Tetrathiafulvalene-Thiacalix[4]arene Conjugates and**  
**Tetrachlorobenzoquinone**

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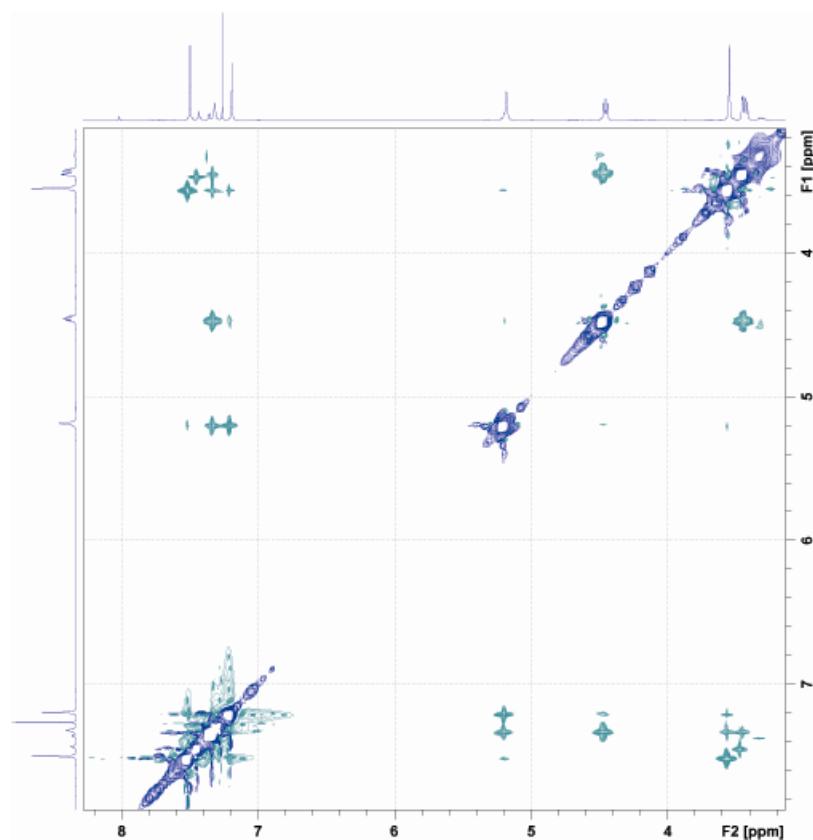


Figure S1. Partial  $^1\text{H}$  NMR NOE spectra of compound **6a**

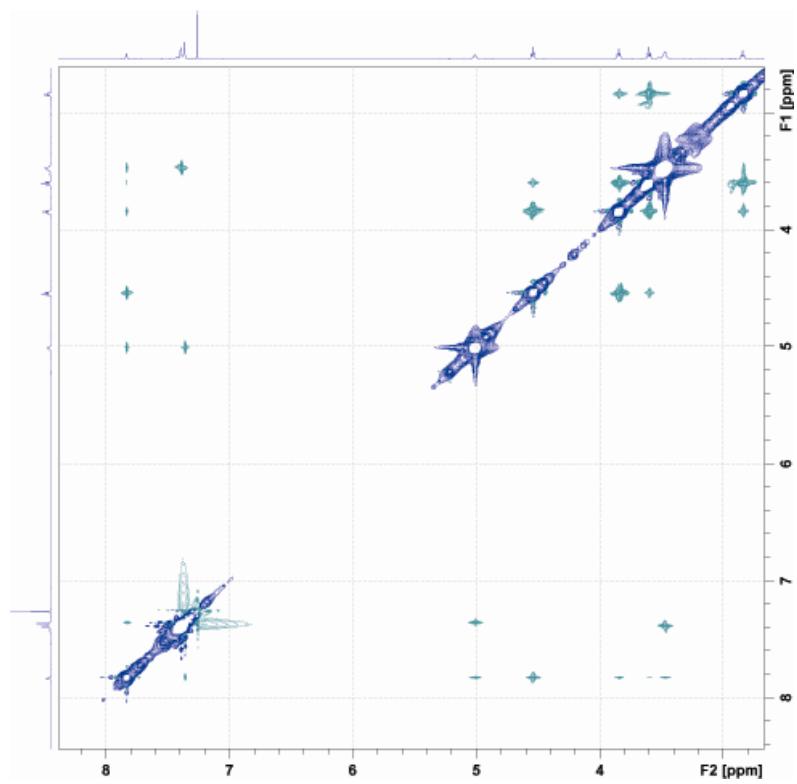


Figure S2. <sup>1</sup>H NMR NOE spectra of compound **6b**

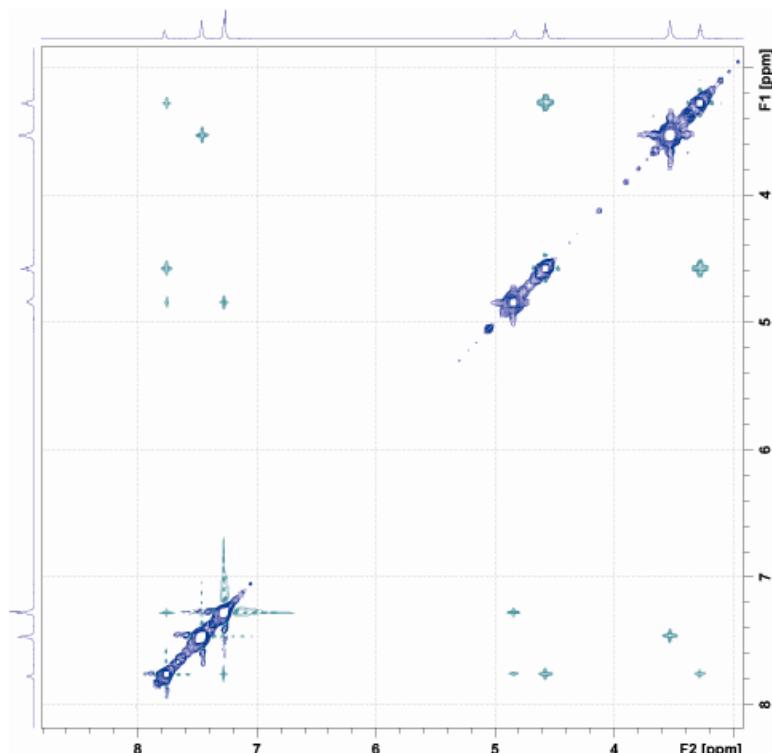


Figure S3. Partial <sup>1</sup>H NMR NOE spectra of compound **7a**

ZXM-27  
20091214-1H  
CDCl<sub>3</sub>

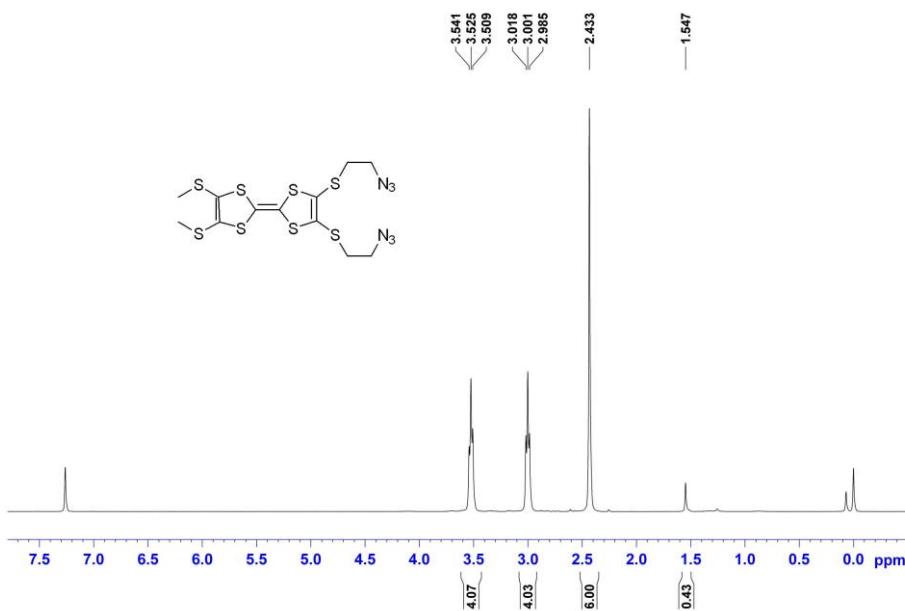


Figure S4. <sup>1</sup>H-NMR spectra of compound 3a

ZXM-27  
20091214-13C  
CDCl<sub>3</sub>

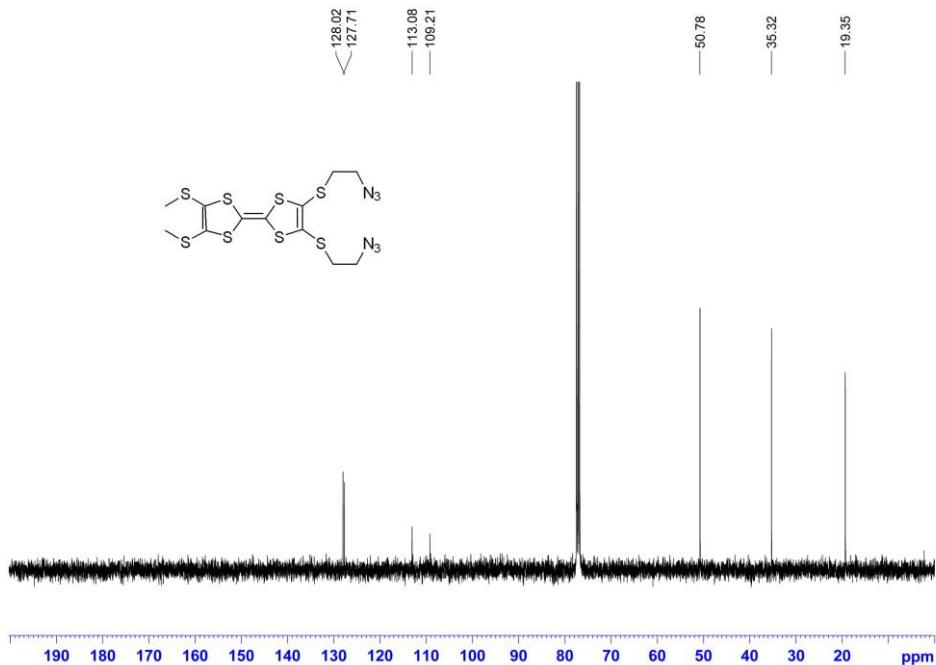


Figure S5. <sup>13</sup>C-NMR spectra of compound 3a

ZXM-31  
20091228-1H  
CDCl<sub>3</sub>

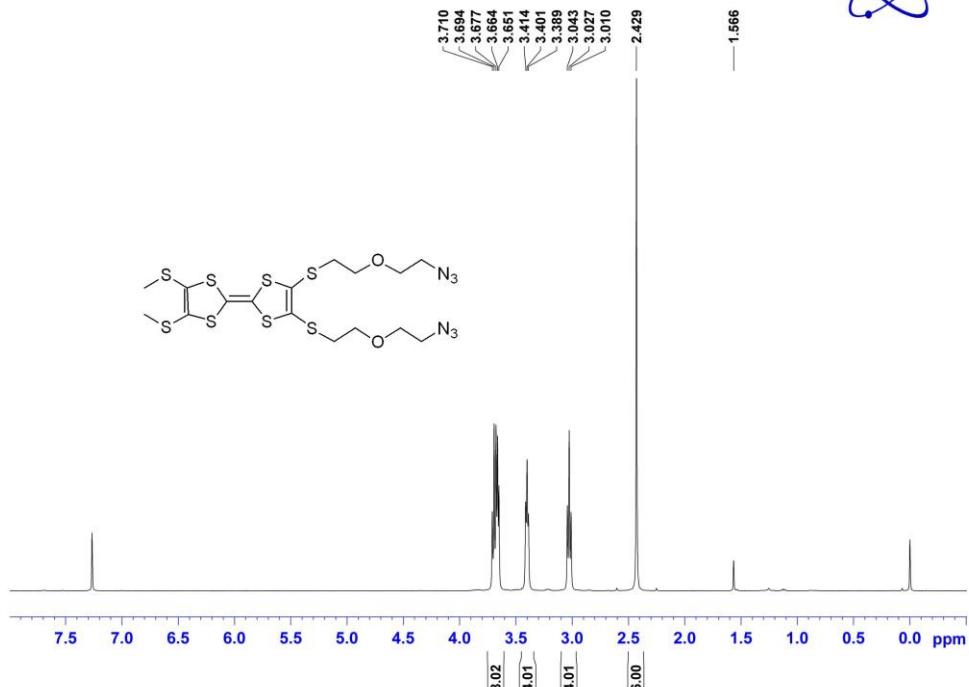


Figure S6. <sup>1</sup>H-NMR spectra of compound 3b

ZXM-31  
20091231-13C  
CDCl<sub>3</sub>

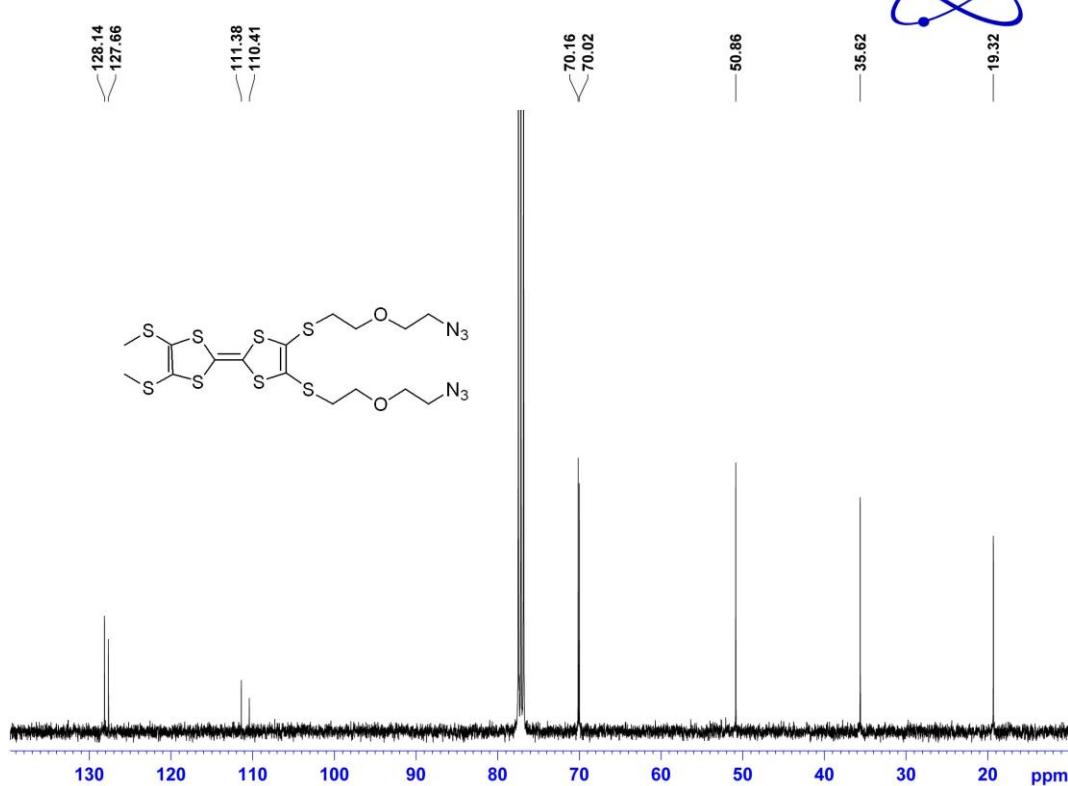


Figure S7. <sup>13</sup>C-NMR spectra of compound 3b

ZXM-33  
20100105-1H  
CDCl<sub>3</sub>

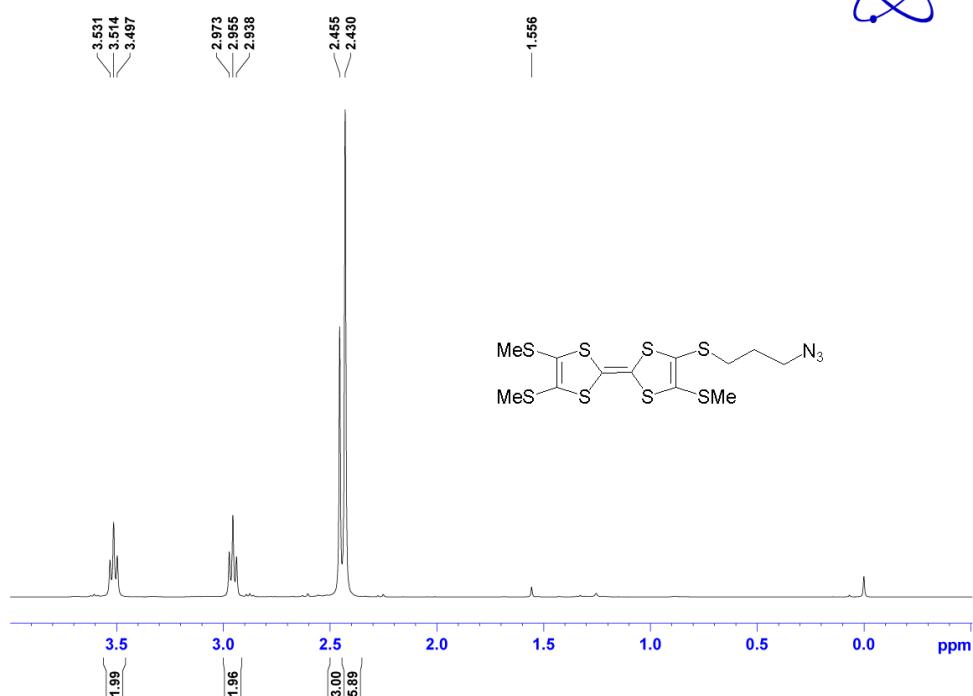


Fig. S8. <sup>1</sup>H-NMR spectra of compound 4a

ZXM-33  
20100106-13C  
CDCl<sub>3</sub>

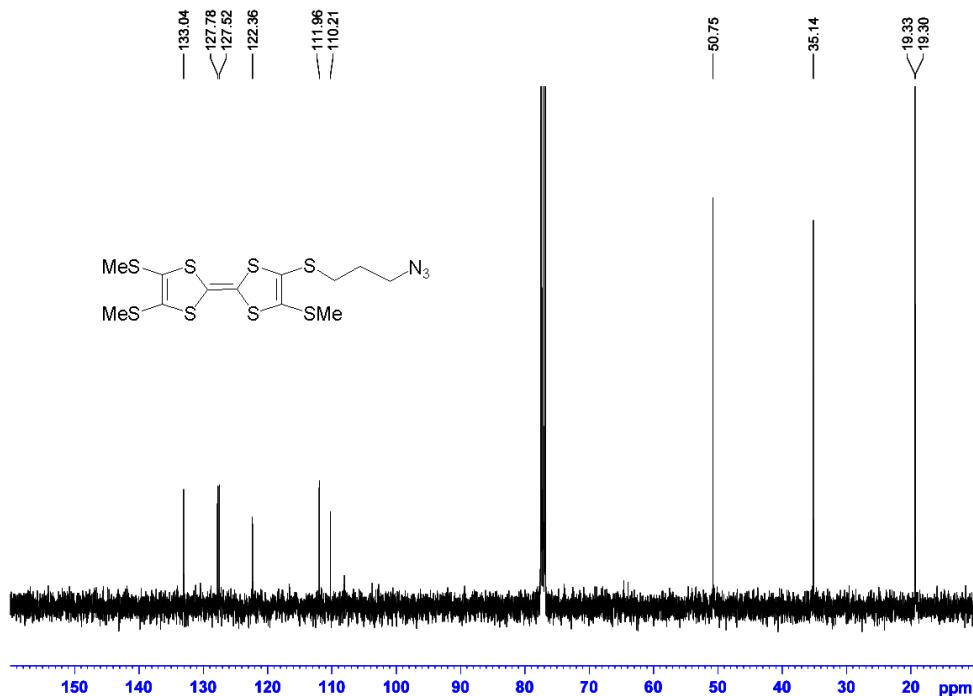


Figure S9. <sup>13</sup>C-NMR spectra of compound 4a

ZXM-35  
20100108-1H  
CDCl<sub>3</sub>

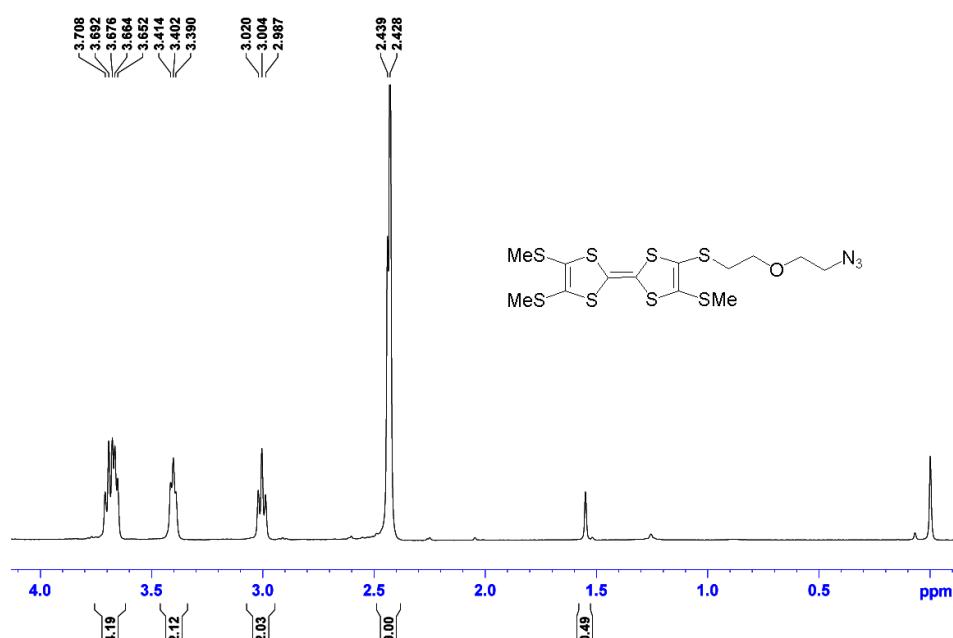


Figure S10. <sup>1</sup>H-NMR spectra of compound 4b

ZXM-35  
20100108-13C  
CDCl<sub>3</sub>

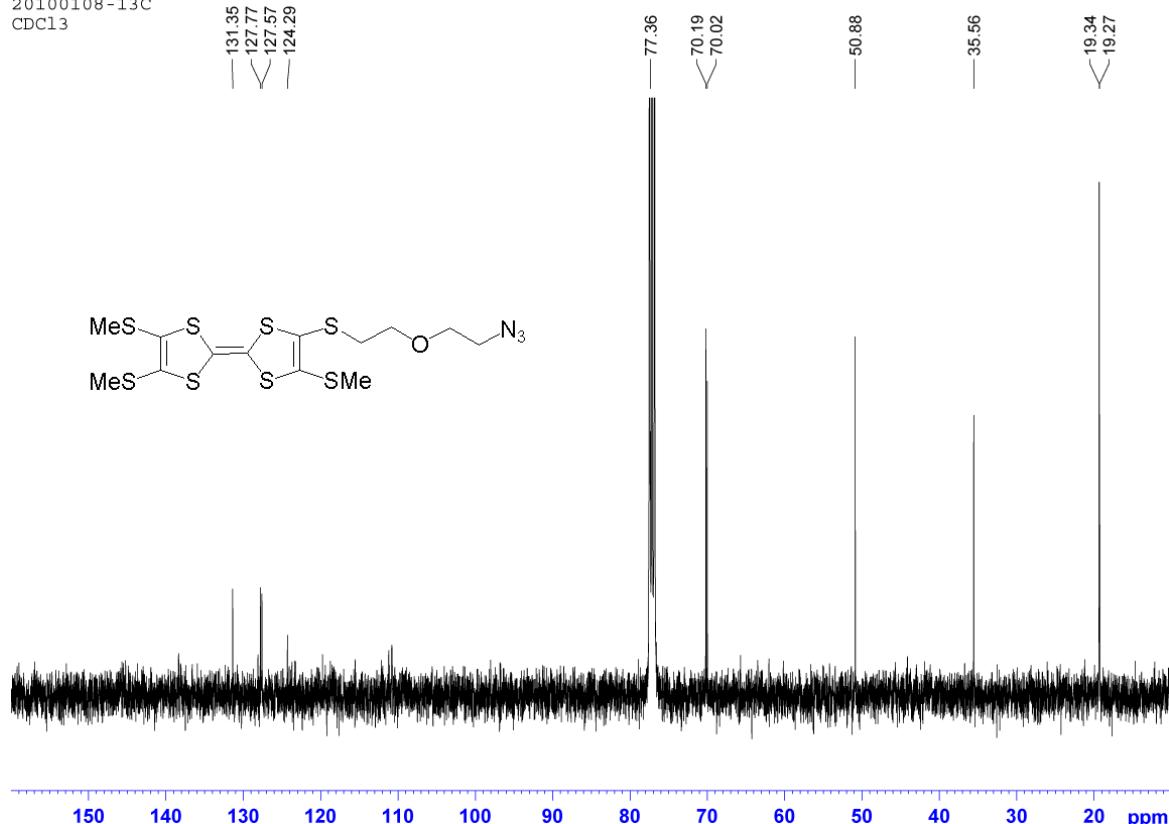


Figure S11. <sup>13</sup>C-NMR spectra of compound 4b



Instrument: Thermo Fisher Scientific LTQ FT Ultra  
 Card Serial Number : M20140580  
 Operator : HUAQIN Date: 2014/11/05  
 Operation Mode: MALDI\_DHB

**Elemental composition search on mass 486.91**

m/z= 481.91-491.91

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
486.9132	486.9132	0.10	7.0	C <sub>13</sub> H <sub>17</sub> O <sub>3</sub> N <sub>3</sub> S <sub>8</sub>
	486.9134	-0.41	23.0	C <sub>20</sub> H <sub>10</sub> O <sub>5</sub> N <sub>5</sub> S <sub>3</sub>
	486.9130	0.48	4.0	C <sub>5</sub> H <sub>13</sub> O <sub>4</sub> N <sub>9</sub> S <sub>7</sub>
	486.9135	-0.49	4.5	C <sub>6</sub> H <sub>11</sub> O <sub>10</sub> N <sub>6</sub> S <sub>5</sub>
	486.9130	0.55	17.0	C <sub>20</sub> H <sub>9</sub> O <sub>4</sub> N <sub>5</sub> S
	486.9136	-0.86	13.0	C <sub>13</sub> H <sub>9</sub> O <sub>2</sub> N <sub>7</sub> S <sub>6</sub>
	486.9137	-0.87	7.5	C <sub>14</sub> H <sub>15</sub> O <sub>7</sub> S <sub>6</sub>
	486.9128	0.92	14.0	C <sub>12</sub> H <sub>5</sub> O <sub>7</sub> N <sub>7</sub> S <sub>4</sub>
	486.9141	-1.83	13.5	C <sub>14</sub> H <sub>7</sub> O <sub>8</sub> N <sub>4</sub> S <sub>4</sub>
	486.9123	1.89	8.0	C <sub>12</sub> H <sub>13</sub> O <sub>6</sub> N <sub>3</sub> S <sub>6</sub>

M20140579 #7 RT: 0.4274 AV: 1 NL: 1.03E4  
 T: FTMS + p MALDI Full ms [150.00-2000.00]

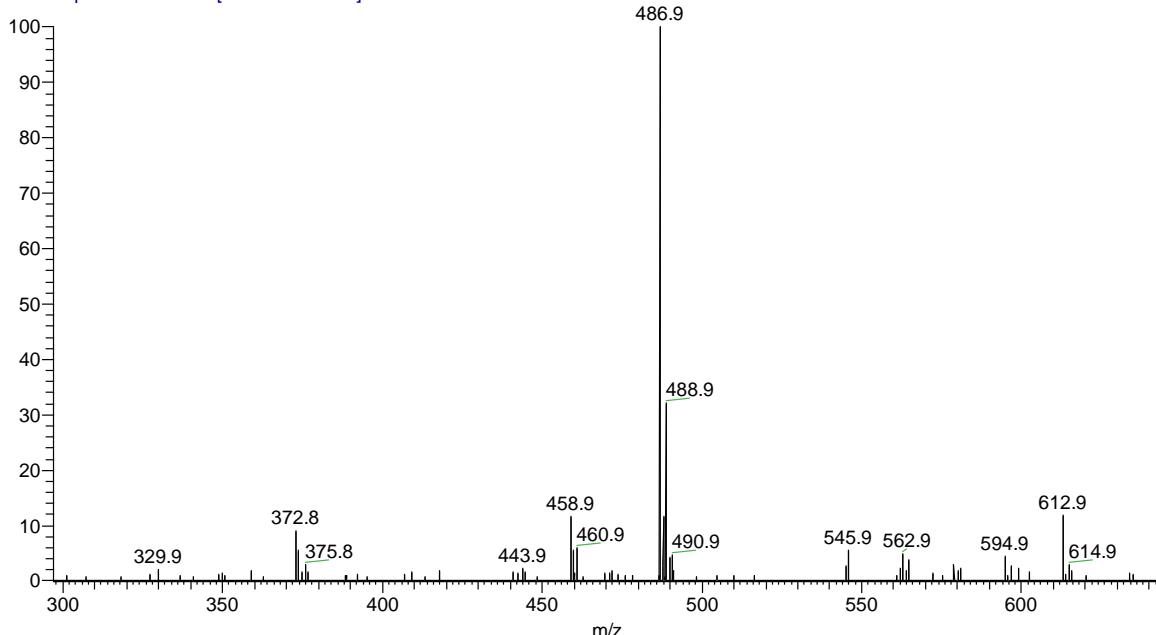


Figure S12. MS spectra report of compound **4b**

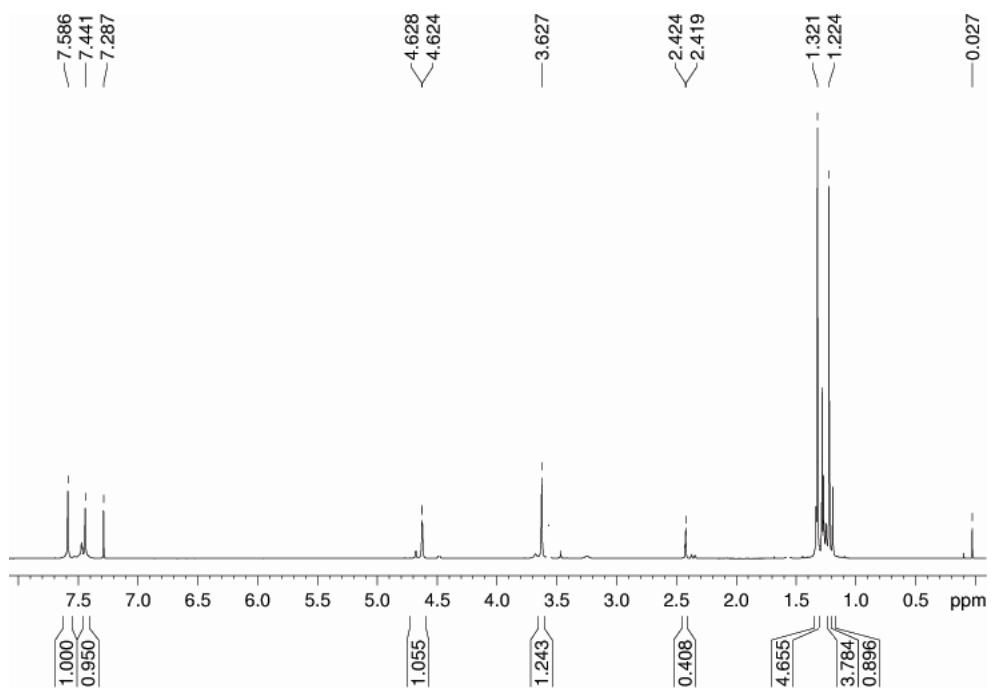


Figure S13. <sup>1</sup>H-NMR spectra of compound 5

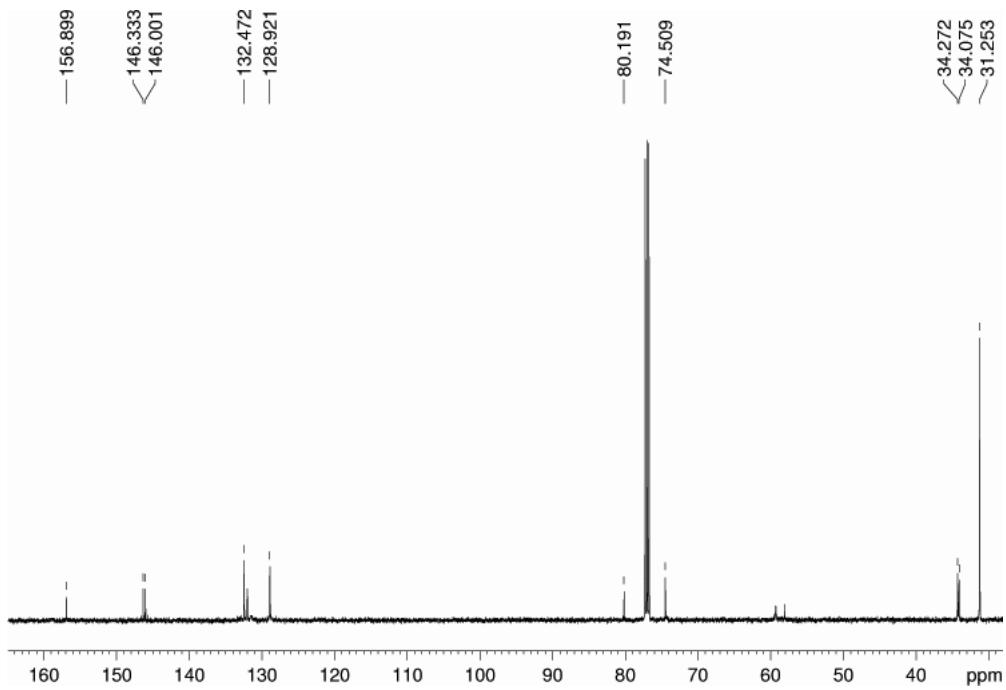


Figure S14. <sup>13</sup>C-NMR spectra of compound 5



Instrument: Thermo Fisher Scientific LTQ FT Ultra

Card Serial Number : M20140582

Operator : HUAQIN

Date: 2014/11/05

Operation Mode: MALDI\_DHB

Elemental composition search on mass 825.31

m/z= 820.31-830.31

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
825.3144	825.3134	1.24	20.5	C <sub>48</sub> H <sub>57</sub> O <sub>4</sub> S <sub>4</sub>
	825.3159	-1.80	16.5	C <sub>44</sub> H <sub>57</sub> O <sub>9</sub> S <sub>3</sub>
	825.3126	2.29	21.5	C <sub>47</sub> H <sub>53</sub> O <sub>9</sub> S <sub>2</sub>
	825.3168	-2.85	15.5	C <sub>45</sub> H <sub>61</sub> O <sub>4</sub> S <sub>5</sub>

M20140581 #10 RT: 0.6355 AV: 1 NL: 1.41E4  
T: FTMS + p MALDI Full ms [150.00-2000.00]

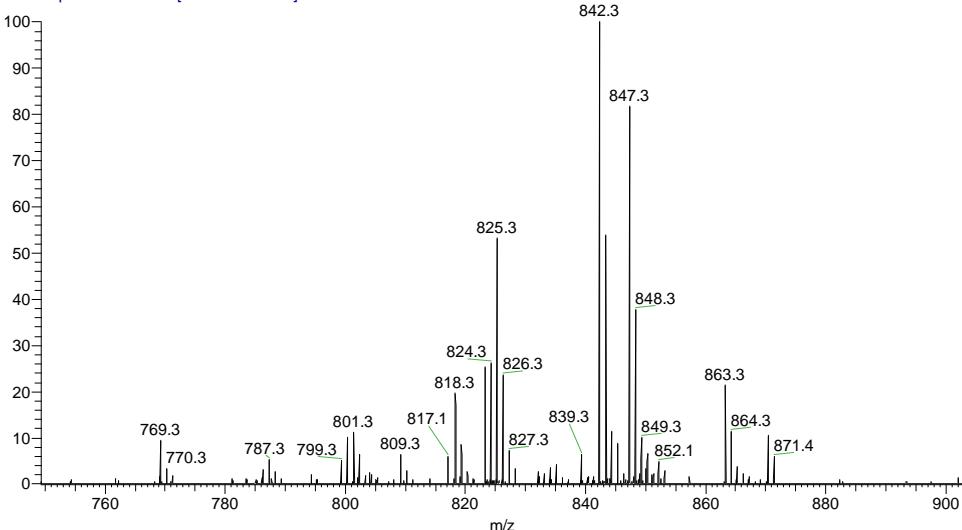


Figure S15. MS spectra report of compound 5

PQM  
20101023-1H  
CDCl<sub>3</sub>

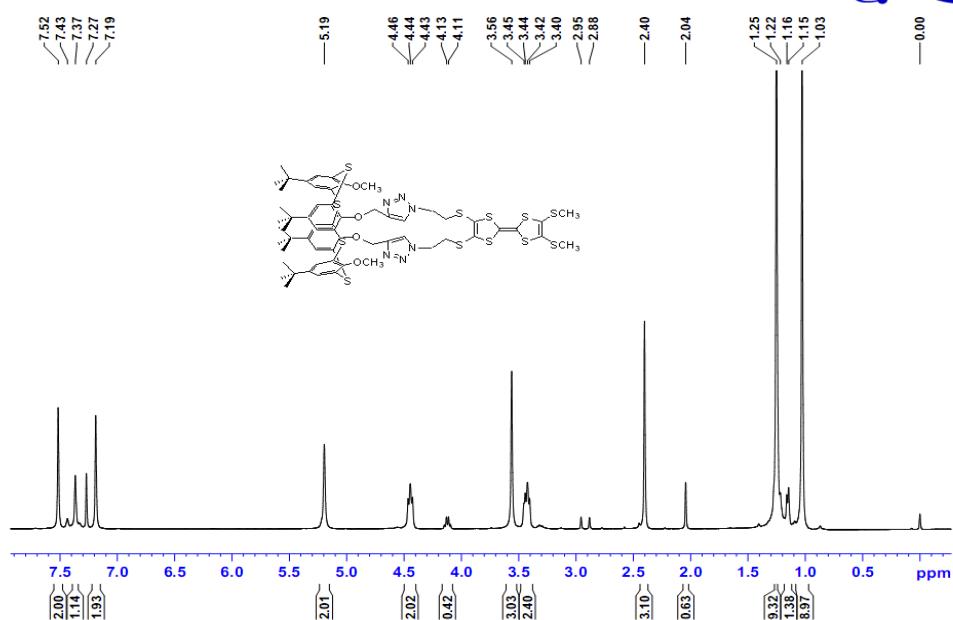


Figure S16. <sup>1</sup>H NMR spectra of compound 6a

PQM-1B  
20101024-13C  
CDCl<sub>3</sub>

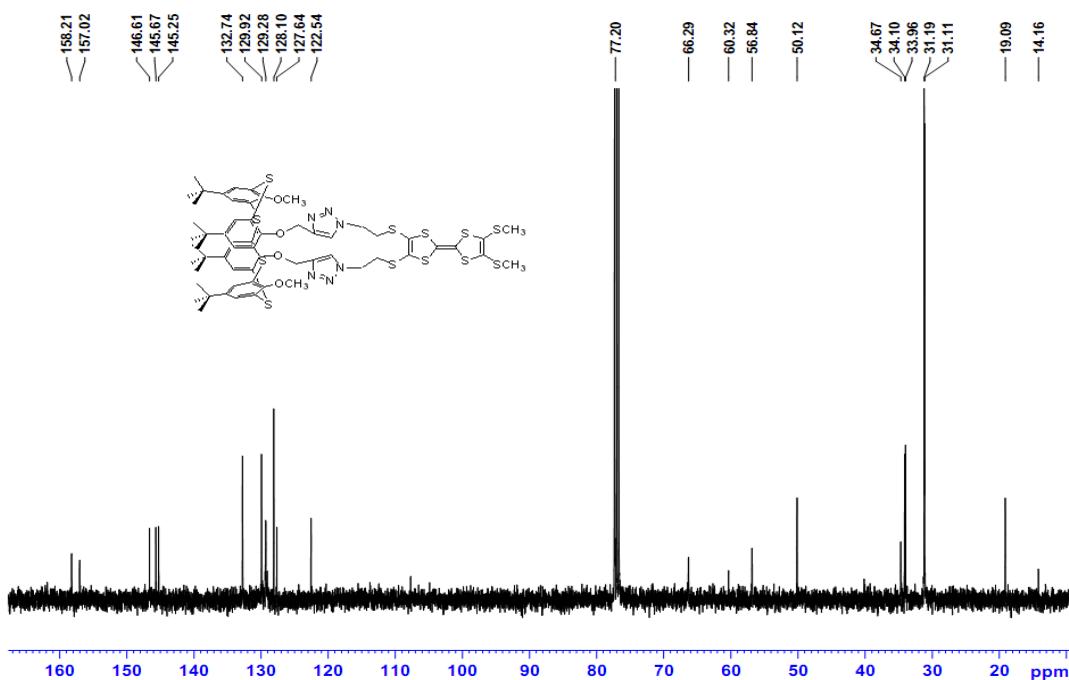


Figure S17. <sup>13</sup>C NMR spectra of compound 6a

National Center for Organic Mass Spectrometry in Shanghai  
 Shanghai Institute of Organic Chemistry  
 Chinese Academic of Sciences  
 High Resolution MS DATA REPORT  
 Sample Serial Number: **6a**



Instrument: Thermo Fisher Scientific LTQ FT Ultra  
 Card Serial Number : M20140575  
 Operator : HUAQIN Date: 2014/11/05  
 Operation Mode: MALDI\_DHB  
 Elemental composition search on mass 1322.21

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
1322.2104	1322.2102	0.17	29.0	C <sub>60</sub> H <sub>70</sub> O <sub>4</sub> N <sub>6</sub> S <sub>12</sub>
	1322.2099	0.33	39.0	C <sub>67</sub> H <sub>62</sub> O <sub>7</sub> N <sub>4</sub> S <sub>9</sub>
	1322.2108	-0.35	19.5	C <sub>54</sub> H <sub>76</sub> O <sub>7</sub> N <sub>5</sub> S <sub>13</sub>
	1322.2111	-0.51	54.0	C <sub>75</sub> H <sub>50</sub> O <sub>6</sub> N <sub>6</sub> S <sub>6</sub>
	1322.2115	-0.84	28.5	C <sub>62</sub> H <sub>72</sub> O <sub>5</sub> N <sub>3</sub> S <sub>12</sub>
	1322.2092	0.86	48.5	C <sub>73</sub> H <sub>56</sub> O <sub>4</sub> N <sub>5</sub> S <sub>8</sub>
	1322.2090	1.02	14.0	C <sub>52</sub> H <sub>82</sub> O <sub>5</sub> N <sub>4</sub> S <sub>15</sub>
	1322.2090	1.02	58.5	C <sub>80</sub> H <sub>48</sub> O <sub>7</sub> N <sub>3</sub> S <sub>5</sub>
	1322.2120	-1.20	34.5	C <sub>62</sub> H <sub>64</sub> O <sub>6</sub> N <sub>7</sub> S <sub>10</sub>
	1322.2086	1.35	39.5	C <sub>65</sub> H <sub>60</sub> O <sub>6</sub> N <sub>7</sub> S <sub>9</sub>

M20140575\_141104153350 #10 RT: 0.5870 AV: 1 NL: 2.95E4  
 T: FTMS + p MALDI Full ms [150.00-2000.00]

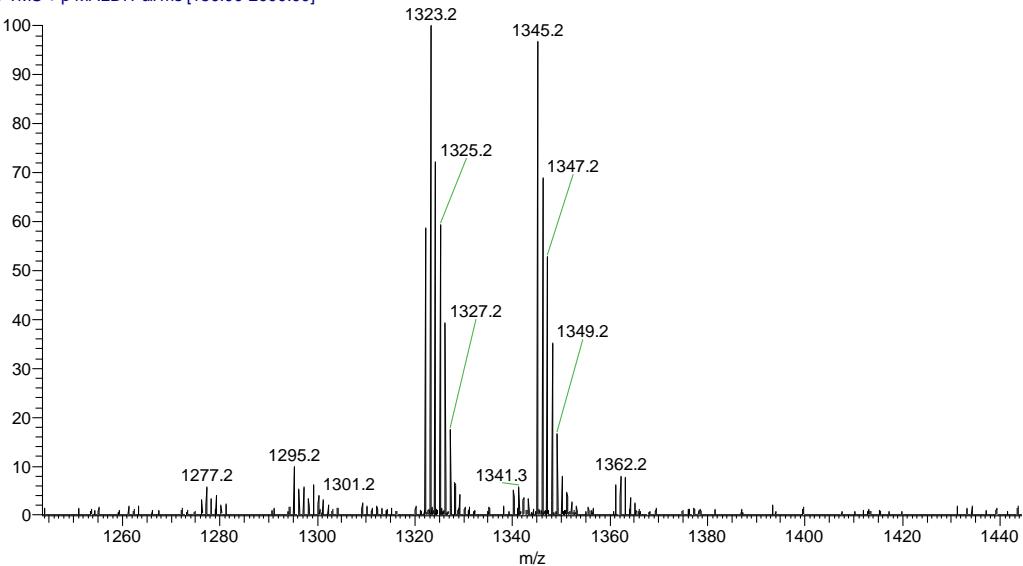


Figure S18. MS spectra report of compound **6a**

PQM-21  
20101209-1H  
CDCl<sub>3</sub>

**BRUKER**

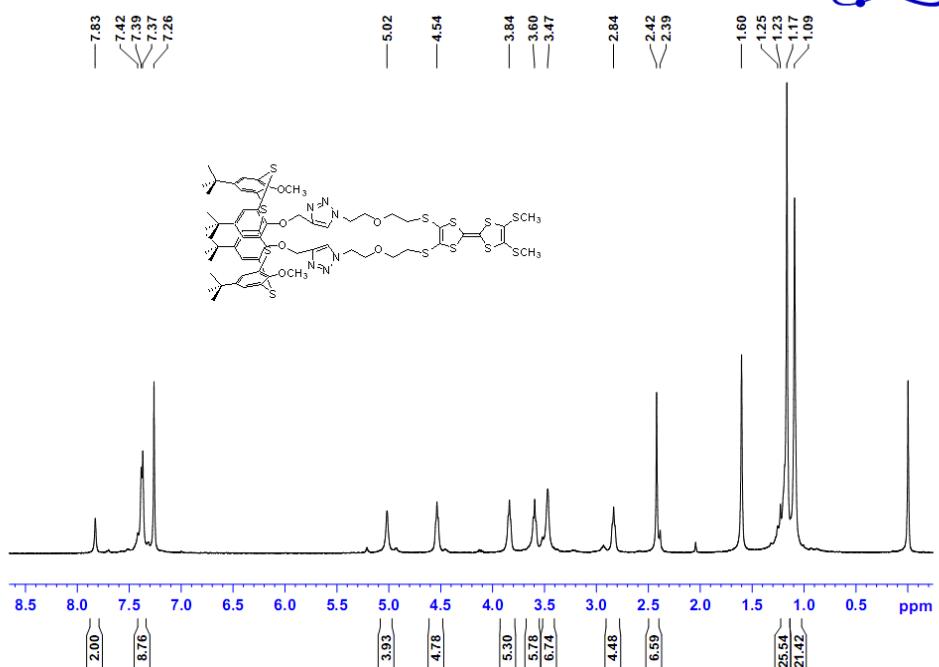


Figure S19. <sup>1</sup>H NMR spectra of compound 6b

PQM-21  
20110113-13C  
CDCl<sub>3</sub>

**BRUKER**

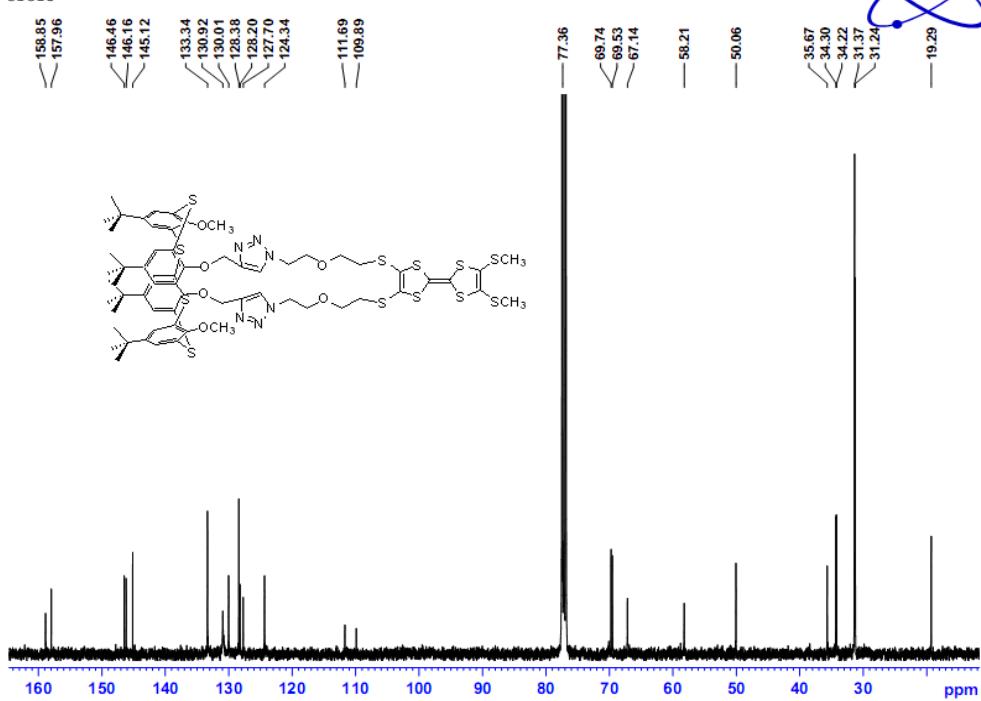


Figure S20. <sup>13</sup>C NMR spectra of compound 6b

National Center for Organic Mass Spectrometry in Shanghai  
 Shanghai Institute of Organic Chemistry  
 Chinese Academic of Sciences  
 High Resolution MS DATA REPORT  
 Sample Serial Number: **6b**



Instrument: Thermo Fisher Scientific LTQ FT Ultra  
 Card Serial Number : M20140577  
 Operator : HUAQIN Date: 2014/11/05  
 Operation Mode: MALDI\_DHB  
 Elemental composition search on mass 1410.27

m/z = 1405.27-1415.27

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
1410.2650	1410.2650	-0.02	43.5	C <sub>74</sub> H <sub>68</sub> O <sub>6</sub> N <sub>5</sub> S <sub>9</sub>
	1410.2653	-0.17	33.5	C <sub>67</sub> H <sub>76</sub> O <sub>3</sub> N <sub>7</sub> S <sub>12</sub>
	1410.2644	0.47	53.0	C <sub>80</sub> H <sub>62</sub> O <sub>3</sub> N <sub>6</sub> S <sub>8</sub>
	1410.2641	0.62	18.5	C <sub>59</sub> H <sub>88</sub> O <sub>4</sub> N <sub>5</sub> S <sub>15</sub>
	1410.2660	-0.66	24.0	C <sub>61</sub> H <sub>82</sub> O <sub>6</sub> N <sub>6</sub> S <sub>13</sub>
	1410.2639	0.78	28.5	C <sub>66</sub> H <sub>80</sub> O <sub>7</sub> N <sub>3</sub> S <sub>12</sub>
	1410.2666	-1.13	33.0	C <sub>69</sub> H <sub>78</sub> O <sub>4</sub> N <sub>4</sub> S <sub>12</sub>
	1410.2632	1.27	38.0	C <sub>72</sub> H <sub>74</sub> O <sub>4</sub> N <sub>4</sub> S <sub>11</sub>
	1410.2673	-1.61	23.5	C <sub>63</sub> H <sub>84</sub> O <sub>7</sub> N <sub>3</sub> S <sub>13</sub>
	1410.2626	1.73	29.0	C <sub>64</sub> H <sub>78</sub> O <sub>6</sub> N <sub>6</sub> S <sub>12</sub>

M20140577 #2 RT: 0.0806 AV: 1 NL: 1.41E4  
 T: FTMS + p MALDI Full ms [150.00-2000.00]

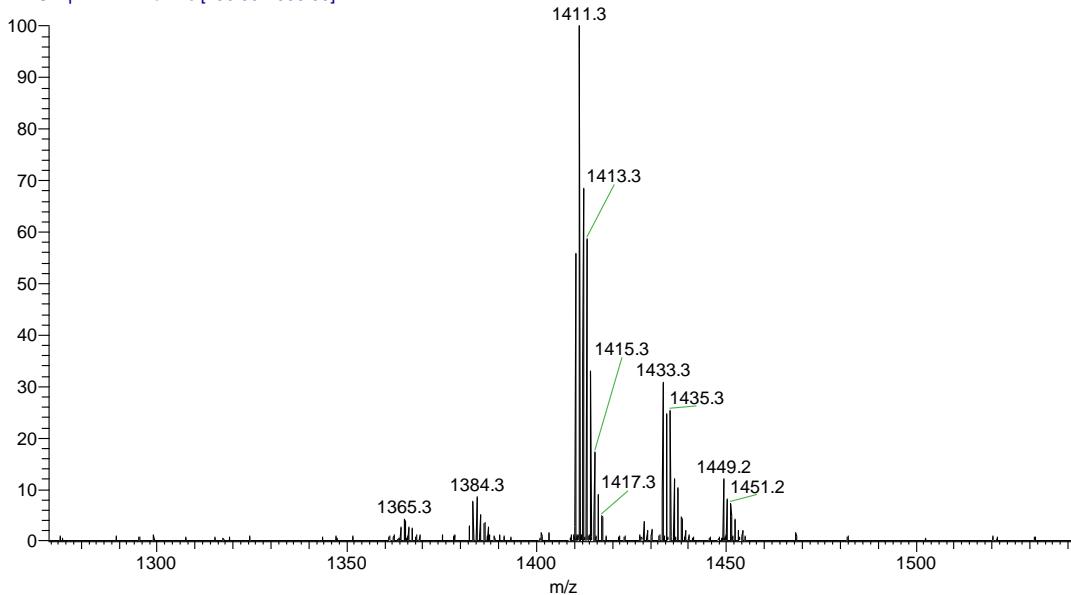


Figure S21. MS spectra report of compound **6b**

PQM-20  
20101103-1H  
CDCl<sub>3</sub>

**BRUKER**

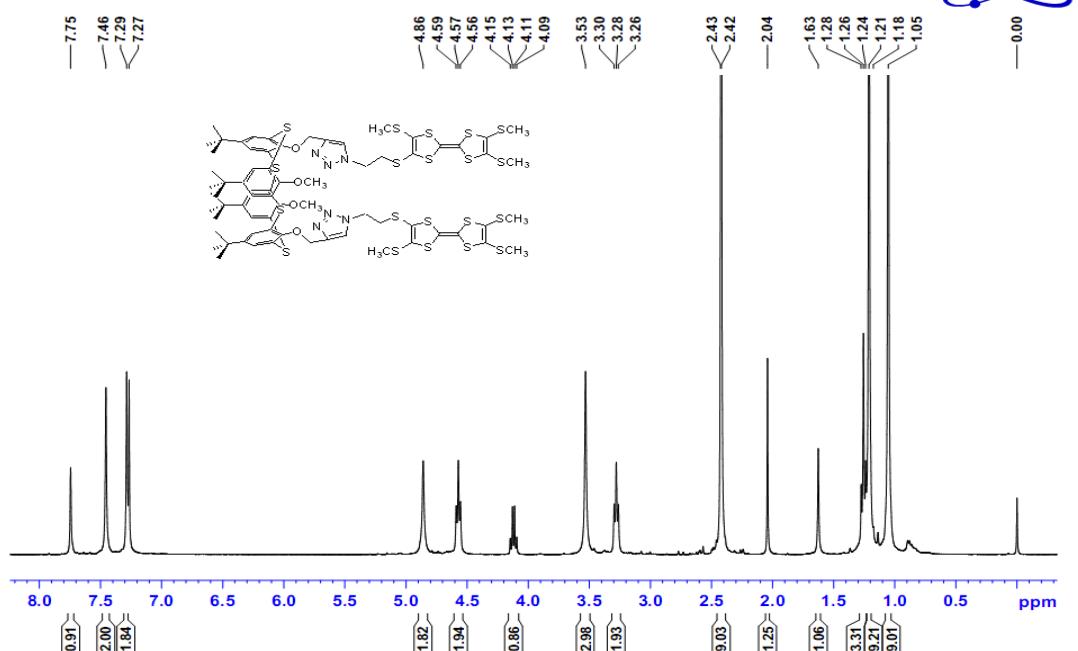


Figure S22. <sup>1</sup>H NMR spectra of compound 7a

PQM-20  
20101103-13C  
CDCl<sub>3</sub>

**BRUKER**

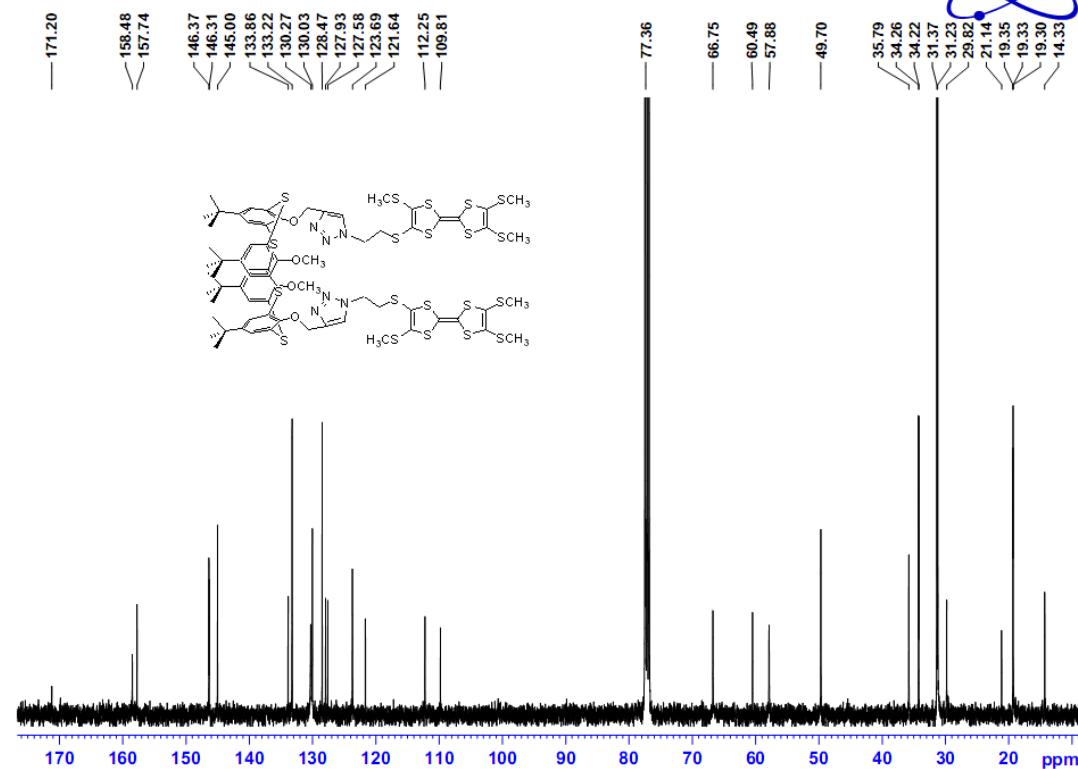


Figure S23. <sup>13</sup>C NMR spectra of compound 7a

Instrument: Thermo Fisher Scientific LTQ FT Ultra  
 Card Serial Number : M20140576  
 Operator : HUAQIN Date: 2014/11/05  
 Operation Mode: MALDI\_DHB

**Elemental composition search on mass 1710.08**

m/z = 1705.08-1715.08

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
1710.0824	1710.0824	-0.04	38.5	C <sub>72</sub> H <sub>76</sub> O <sub>6</sub> N <sub>7</sub> S <sub>18</sub>
	1710.0820	0.24	32.5	C <sub>72</sub> H <sub>84</sub> O <sub>5</sub> N <sub>3</sub> S <sub>20</sub>
	1710.0831	-0.42	47.5	C <sub>80</sub> H <sub>72</sub> O <sub>4</sub> N <sub>5</sub> S <sub>17</sub>
	1710.0838	-0.82	38.0	C <sub>74</sub> H <sub>78</sub> O <sub>7</sub> N <sub>4</sub> S <sub>18</sub>
	1710.0806	1.02	33.0	C <sub>70</sub> H <sub>82</sub> O <sub>4</sub> N <sub>6</sub> S <sub>20</sub>
	1710.0804	1.15	43.0	C <sub>77</sub> H <sub>74</sub> O <sub>7</sub> N <sub>4</sub> S <sub>17</sub>
	1710.0791	1.93	43.5	C <sub>75</sub> H <sub>72</sub> O <sub>6</sub> N <sub>7</sub> S <sub>17</sub>
	1710.0858	-2.01	33.5	C <sub>69</sub> H <sub>80</sub> O <sub>6</sub> N <sub>7</sub> S <sub>19</sub>
	1710.0786	2.21	37.5	C <sub>75</sub> H <sub>80</sub> O <sub>5</sub> N <sub>3</sub> S <sub>19</sub>
	1710.0865	-2.39	42.5	C <sub>77</sub> H <sub>76</sub> O <sub>4</sub> N <sub>5</sub> S <sub>18</sub>

M20140576\_141104153350 #3 RT: 0.1409 AV: 1 NL: 5.80E3  
 T: FTMS + p MALDI Full ms [150.00-2000.00]

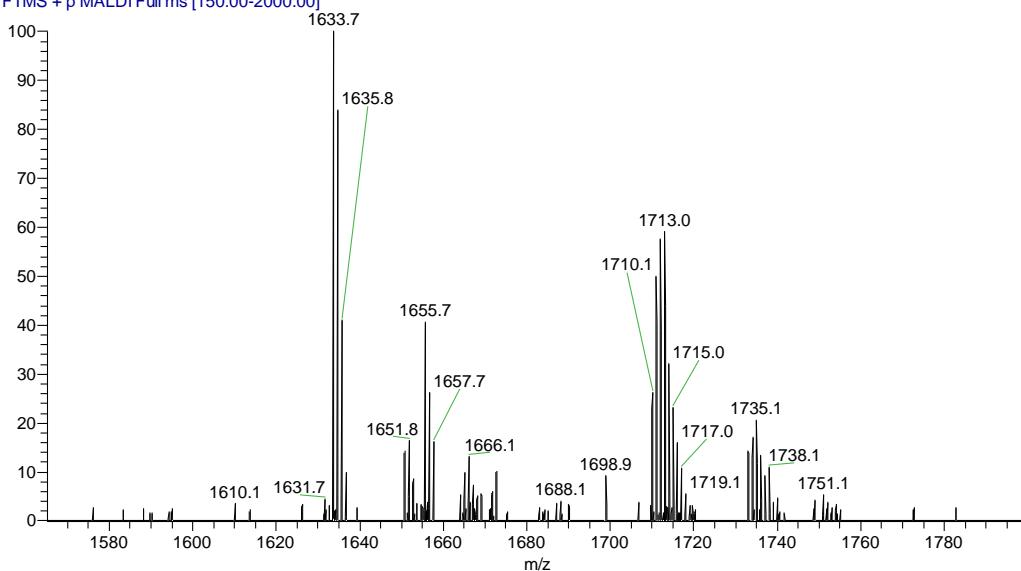


Figure S24. MS spectra report of compound **7a**

PQM-22  
20101209-1H  
CDC13

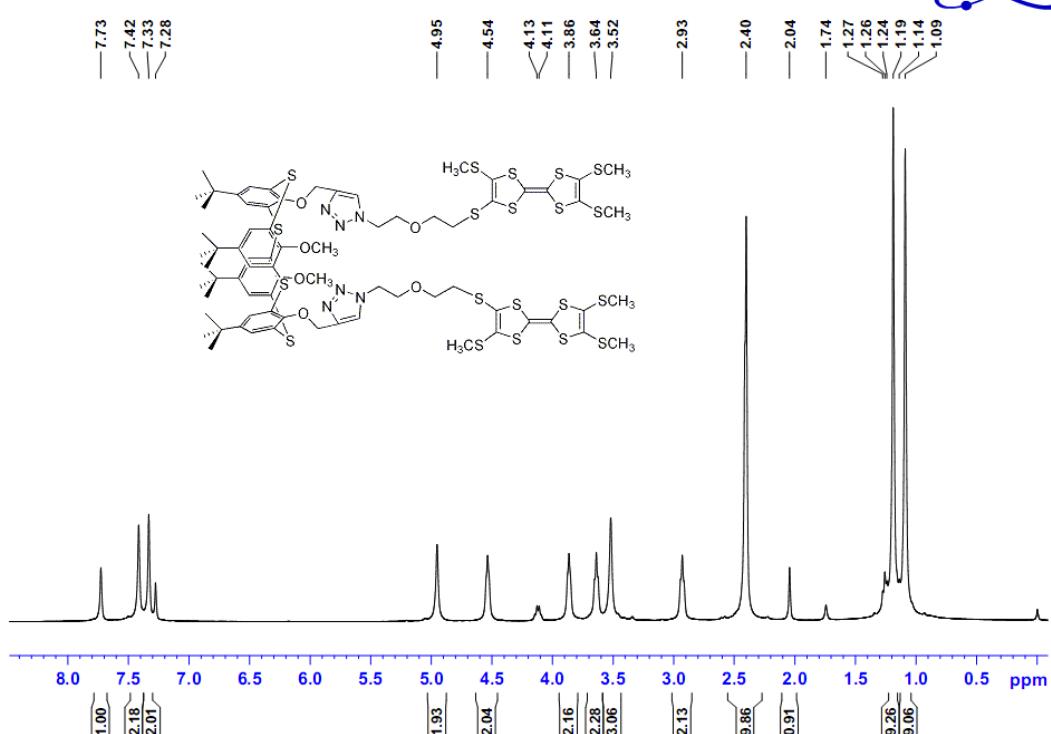


Figure S25. <sup>1</sup>H NMR spectra of compound 7b

PQM-22  
20101209-13C  
CDC13

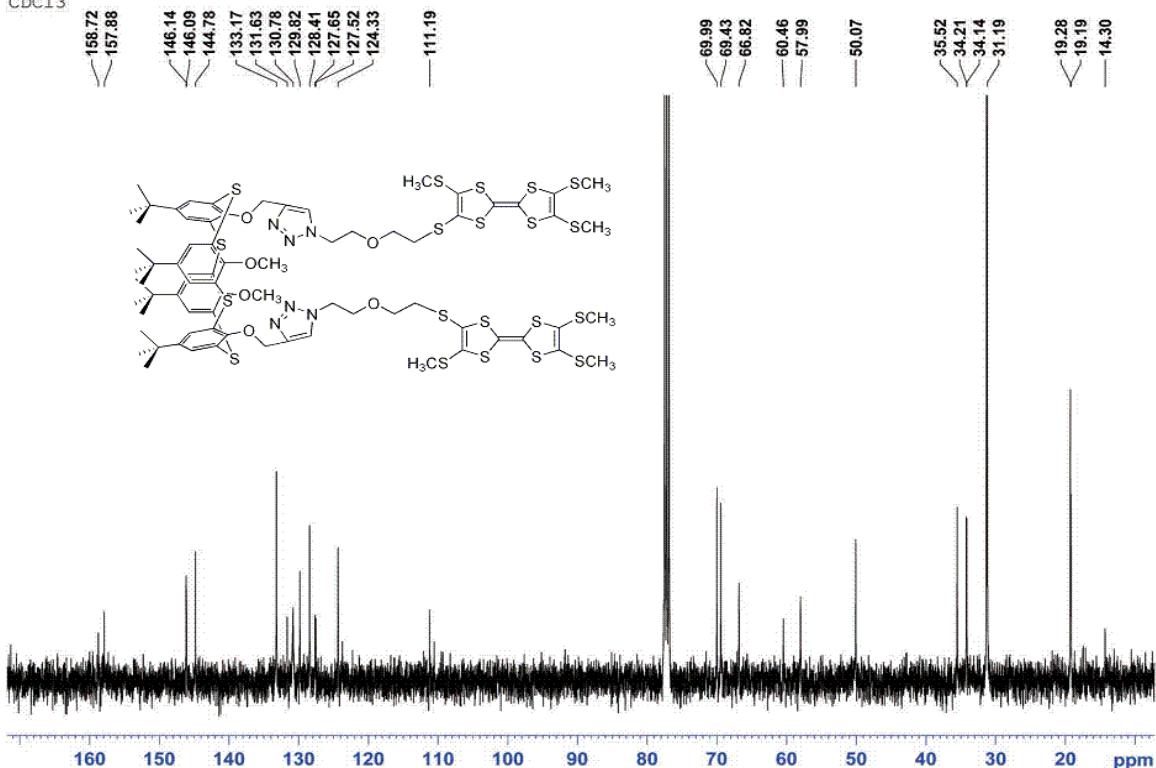


Figure S26. <sup>13</sup>C NMR spectra of compound 7b

National Center for Organic Mass Spectrometry in Shanghai  
 Shanghai Institute of Organic Chemistry  
 Chinese Academic of Sciences  
 High Resolution MS DATA REPORT  
 Sample Serial Number: **7b**



Instrument: Thermo Fisher Scientific LTQ FT Ultra

Card Serial Number : M20140578

Operator : HUAQIN

Date: 2014/11/05

Operation Mode: MALDI\_DHB

Elemental composition search on mass 1798.14

m/z= 1793.14-1803.14

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
1798.1366	1798.1371	-0.25	37.0	C <sub>79</sub> H <sub>90</sub> O <sub>4</sub> N <sub>4</sub> S <sub>20</sub>
	1798.1357	0.49	37.5	C <sub>77</sub> H <sub>88</sub> O <sub>3</sub> N <sub>7</sub> S <sub>20</sub>
	1798.1344	1.24	32.5	C <sub>76</sub> H <sub>92</sub> O <sub>7</sub> N <sub>3</sub> S <sub>20</sub>
	1798.1330	1.99	33.0	C <sub>74</sub> H <sub>90</sub> O <sub>6</sub> N <sub>6</sub> S <sub>20</sub>
	1798.1324	2.37	42.5	C <sub>80</sub> H <sub>84</sub> O <sub>3</sub> N <sub>7</sub> S <sub>19</sub>
	1798.1310	3.11	37.5	C <sub>79</sub> H <sub>88</sub> O <sub>7</sub> N <sub>3</sub> S <sub>19</sub>
	1798.1423	-3.13	37.5	C <sub>78</sub> H <sub>88</sub> O <sub>6</sub> N <sub>5</sub> S <sub>19</sub>
	1798.1297	3.86	38.0	C <sub>77</sub> H <sub>86</sub> O <sub>6</sub> N <sub>6</sub> S <sub>19</sub>

M20140578 #43 RT: 2.8756 AV: 1 NL: 1.45E3  
 T: FTMS + p MALDI Full ms [150.00-2000.00]

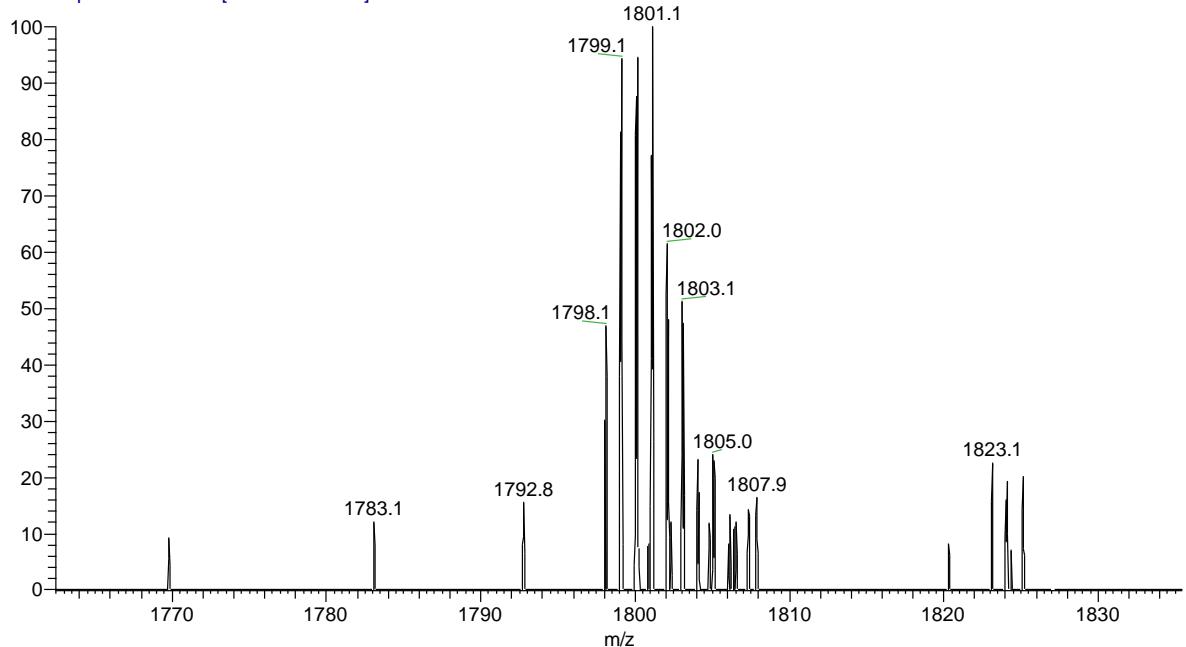
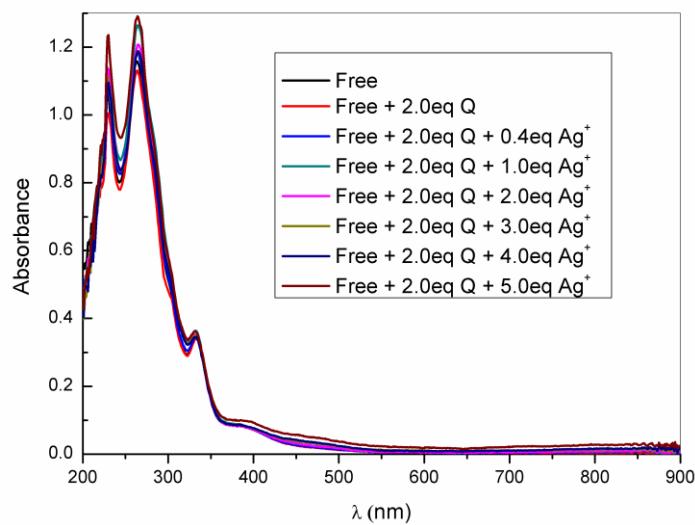
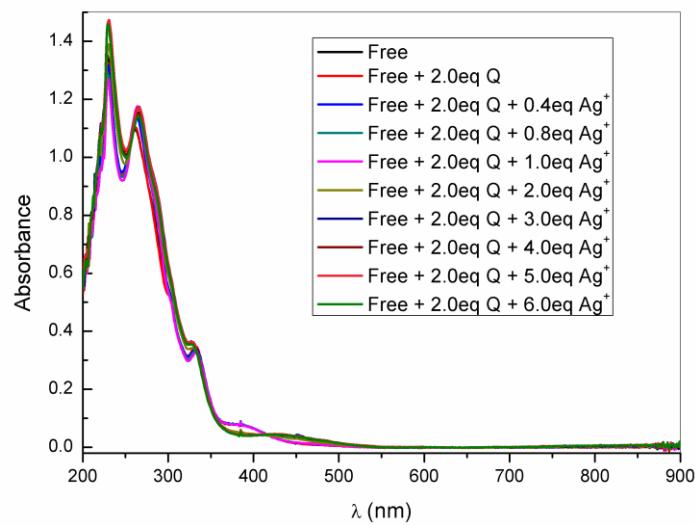


Figure S27. MS spectra report of compound **7b**

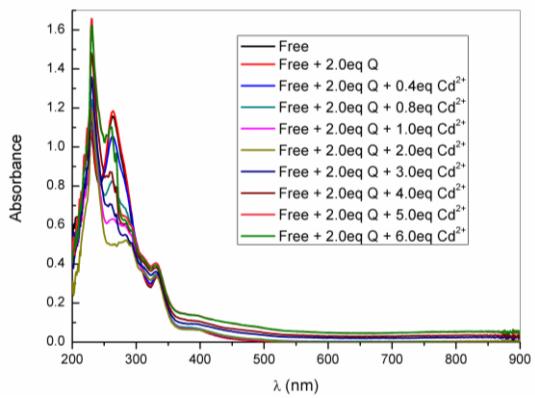


**6a**

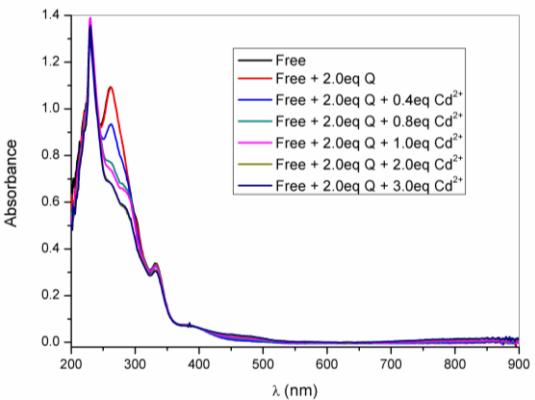


**6b**

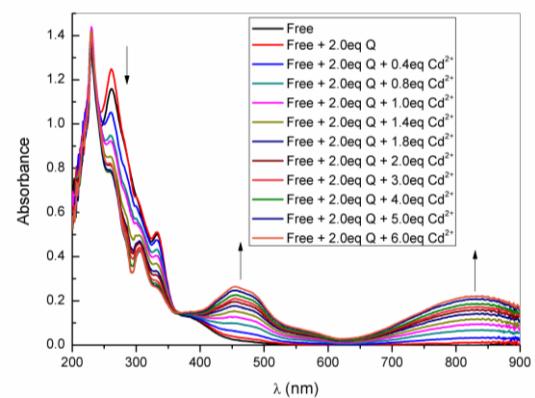
Figure S28. The spectra changes of TTF-TCA compounds **6a** (up) and **6b** (down) ( $5.0 \times 10^{-5}$  M) in the presence Q ( $1.0 \times 10^{-4}$  M) upon addition of different equiv.  $\text{Ag}^+$  ions in  $\text{CH}_3\text{CN}-\text{CH}_2\text{Cl}_2$  (V/V = 1:1)



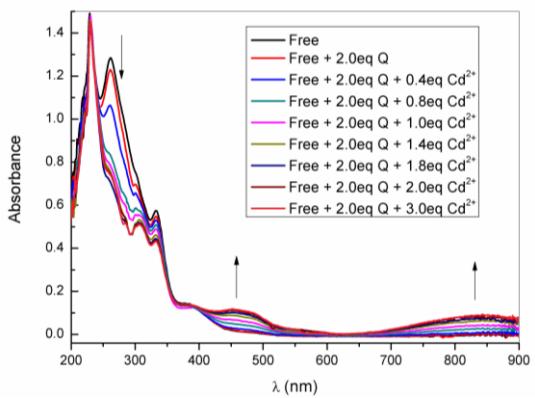
**6a**



**6b**

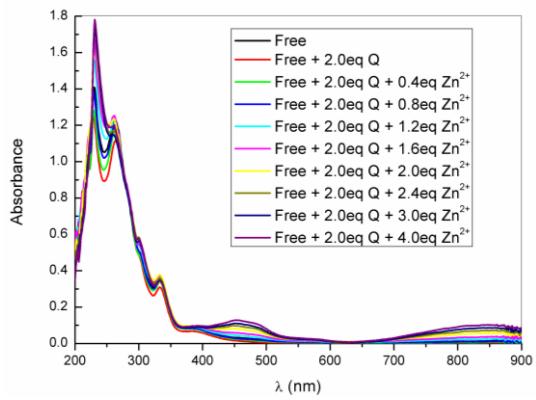


**7a**

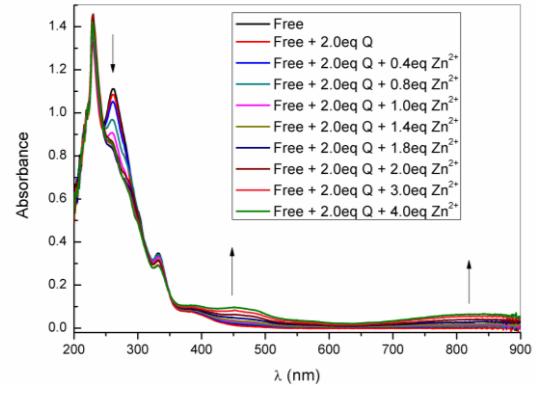


**7b**

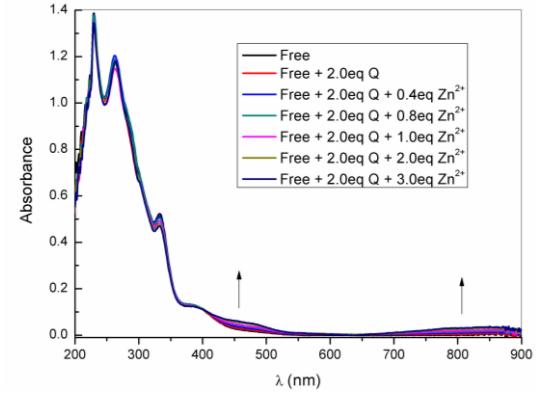
Figure S29. The spectra changes of TTF-TCA compounds **6a**, **6b**, **7a** and **7b** ( $5.0 \times 10^{-5}$  M) in the presence Q ( $1.0 \times 10^{-4}$  M) upon addition of different equiv.  $\text{Cd}^{2+}$  ions in  $\text{CH}_3\text{CN}-\text{CH}_2\text{Cl}_2$  (V/V = 1:1)



**6a**



**6b**



**7a**

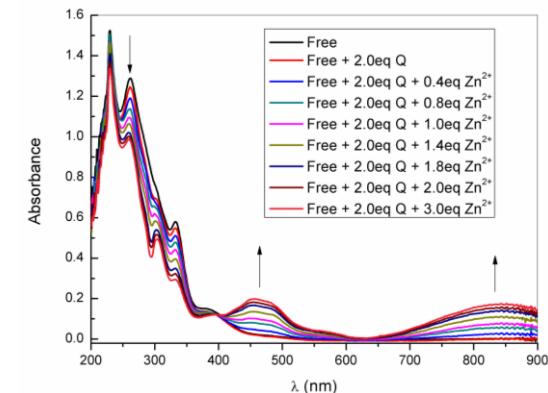
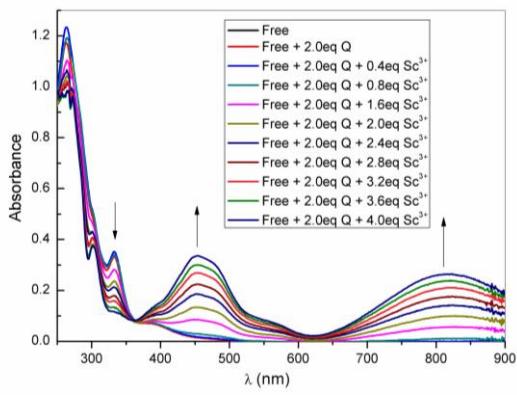
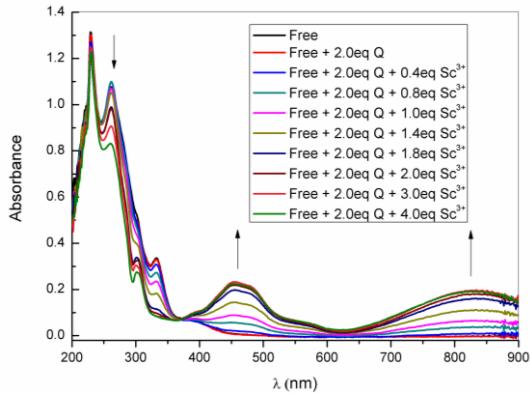


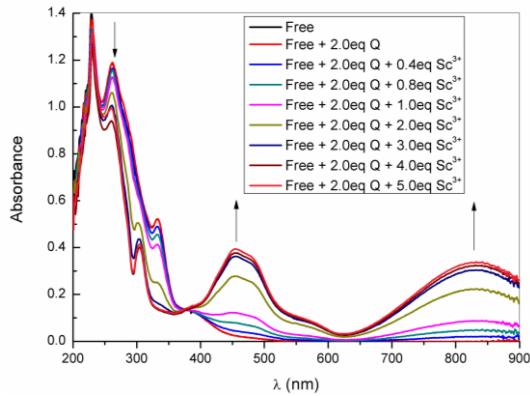
Figure S30. The spectra changes of TTF-TCA compounds **6a**, **6b**, **7a** and **7b** ( $5.0 \times 10^{-5}$  M) in the presence Q ( $1.0 \times 10^{-4}$  M) upon addition of different equiv. Cd<sup>2+</sup> ions in CH<sub>3</sub>CN-CH<sub>2</sub>Cl<sub>2</sub> (V/V = 1:1)



6a



6b



7a

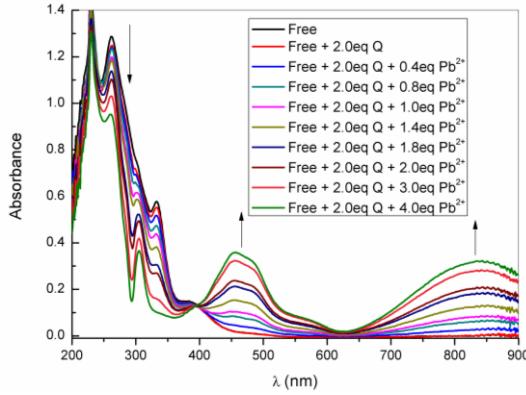
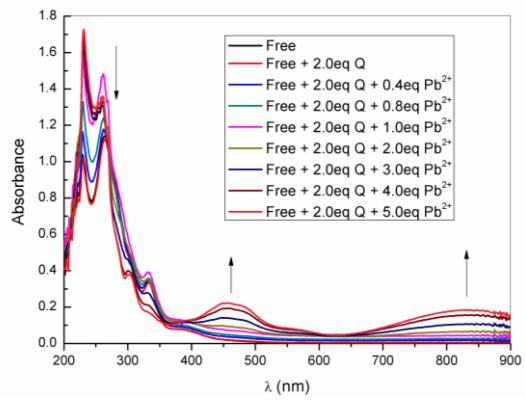
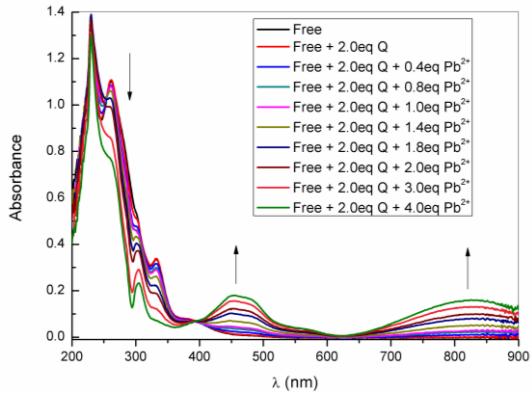


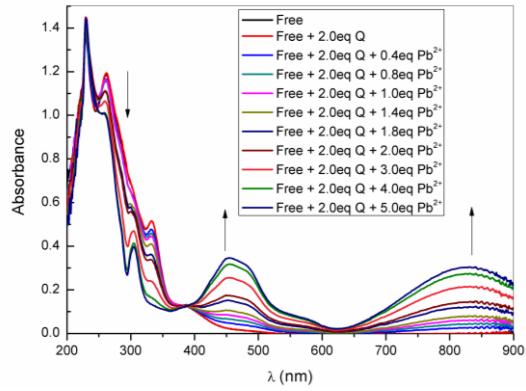
Figure S31. The spectra changes of TTF-TCA compounds **6a**, **6b**, **7a** and **7b** ( $5.0 \times 10^{-5}$  M) in the presence Q ( $1.0 \times 10^{-4}$  M) upon addition of different equiv.  $\text{Sc}^{3+}$  ions in  $\text{CH}_3\text{CN}-\text{CH}_2\text{Cl}_2$  (V/V = 1:1)



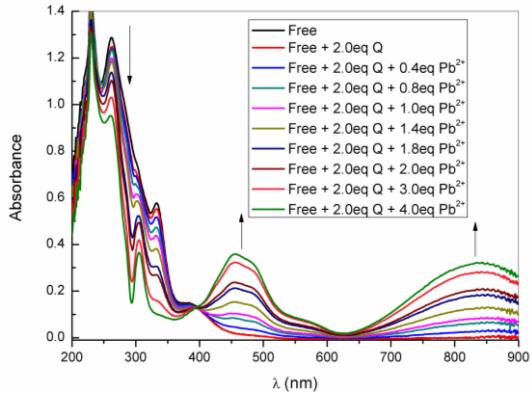
**6a**



**6b**

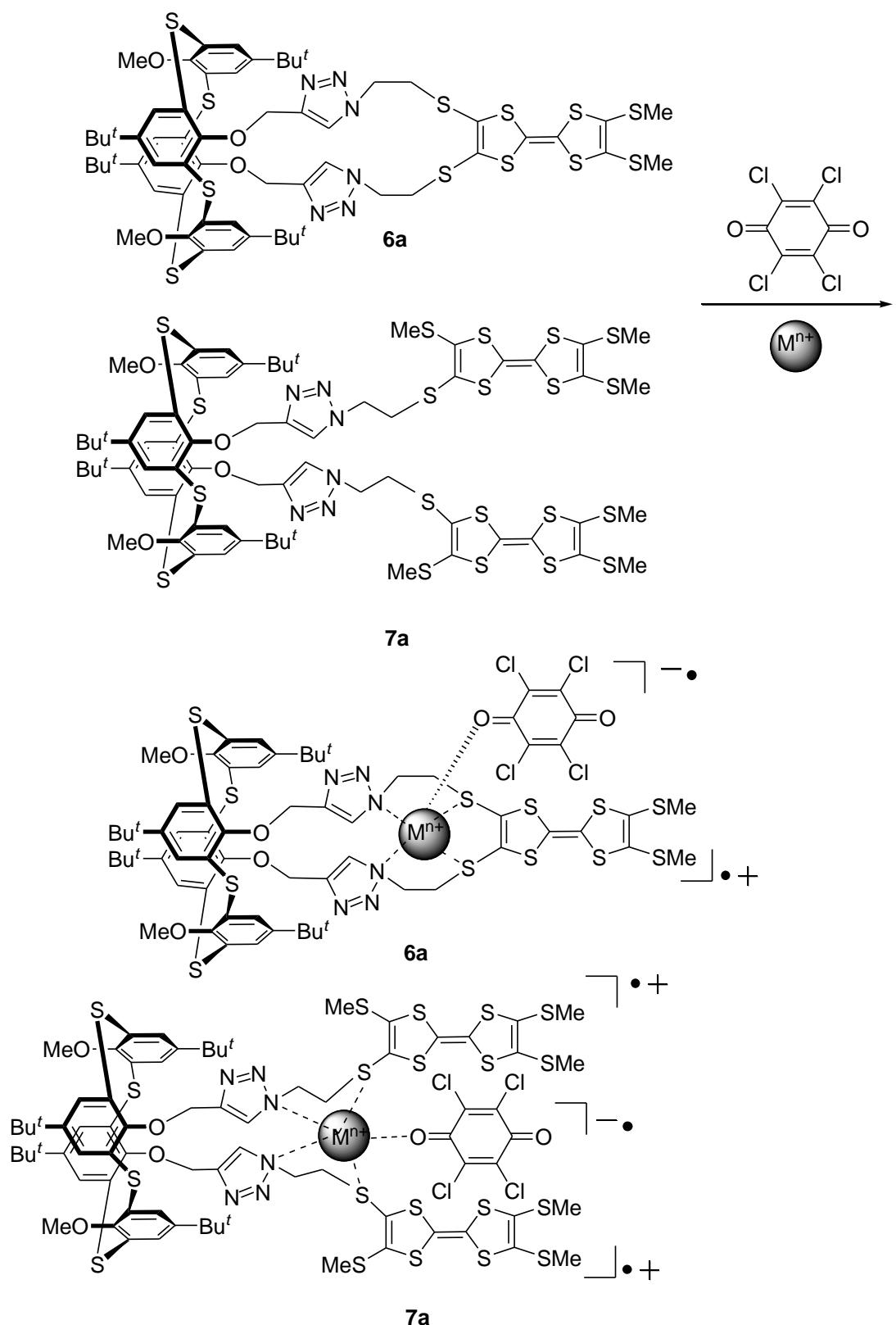


**7a**



**7b**

Figure S32. The spectra changes of TTF-TCA compounds **6a**, **6b**, **7a** and **7b** ( $5.0 \times 10^{-5}$  M) in the presence Q ( $1.0 \times 10^{-4}$  M) upon addition of different equiv. Pb<sup>2+</sup> ions in CH<sub>3</sub>CN-CH<sub>2</sub>Cl<sub>2</sub> (V/V = 1:1)



Scheme S1. Plausible mode of intermolecular electron transfer between TTF-TCA **6a** or **7a** and  $Q$  mediated by the added metal ions.