Electronic Supplementary Information

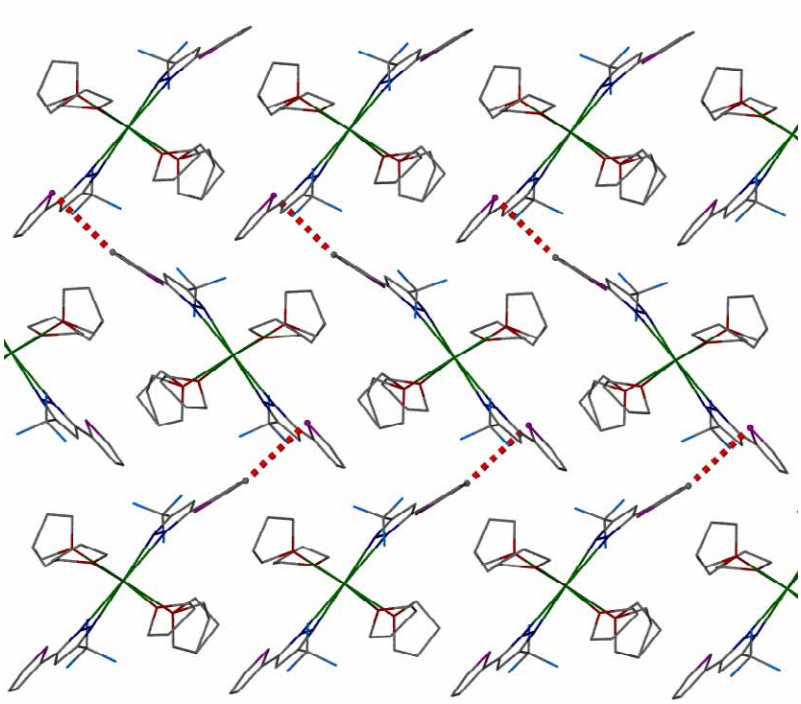

Figure S1: Intermolecular CH...S edge-to-face interactions in complexes **1-4** highlighted as red dashed lines. View down the b axis.

Full variata for complexes **1-8**:

[Yb(ttfpz)$_2$(thf)$_4$] (1):

Thiophene groups were disordered over two positions, their occupancies were freely refined against each other (45:55 for S(1) and 70:30 for S(2)). Both parts of the disordered groups were restrained using DFIX and DANG commands. Both components of the disorder of thiophene S(2) were restrained using SIMU. Two of the thf ligands (O(1) and O(3)) were also disordered over two positions. Their occupancies were freely refined against each other (62:38 and 70:30). The TWIN command was employed and the BASF factor was refined to be approximately 0.15.

[Ca(ttfpz)$_2$(thf)$_4$] (2):

Thiophene groups were disordered over two positions, their occupancies were freely refined against each other (48:52 for S(1) and 70:30 for S(2)). Both parts of the disordered groups were restrained using DFIX and DANG commands, they were also FLATtened. EADP constraints were applied on disordered atoms C(5) and C(13A) with atoms C(5A) and C(13) respectively used as reference. Thiophene rings S(1), S(1A) and S(2A) were also restrained using SIMU. Thf-molecules O(1,2 and 3) were also disordered and the occupancies of the involved atoms were freely refined against each other

(refined occupancies were 40:60 (O(1)), 70:30 (O(2)) and 52:48 (O(3))). SIMU and DFIX restraints were also applied on some involved atoms. Additionally, the structure was inverted.

[Sr(ttfpz)$_2$(thf)$_4$] (3):

Thiophene groups were disordered over two positions, their occupancies were freely refined against each other (59:41 for S(1) and 76:24 for S(2)). Both disordered groups were restrained using the SIMU command. SIMU was also applied on thf molecules O(1) and O(3). Carbon atoms C(25) and C(26) of thf molecule O(3) are disordered over two positions, their occupancy was freely refined against each other (64:36). The distance between C(23) and C(24) was restrained using the DFIX command. The distance between C(14A) and C(15A) was restrained using the SADI command using atoms C(6) and C(7) as reference.

[Ba(ttfpz)$_2$(thf)$_4$] (4):

Thiophene groups S(1) and S(2) and molecule thf O(1) were restrained using SIMU. C-C and C-S distances in thiophene S(1) were restrained with DFIX and DANG on atoms C(4), C(5) and C(5), S(1) respectively. Atoms C(23) and C(24) as well as atoms C(25) and C(26) of thf-molecules O(2) and O(3) respectively are disordered over two positions, their occupancies were refined to be approximately 60:40 and 56:44 respectively. Additionally, the TWIN command was used and the BASF value was refined to be 0.53.

[Ca(ttfpz)$_2$(dme)$_2$] (5):

The EADP constraint was applied on atom C(13), with atom C(5) as reference.

[Sr(ttfpz)$_2$(dme)$_2$] (6):

The data set showed twinning. Initial indexing for the two components of the twin was carried out using CELL NOW within the APEX2 software package.[69] Multi-component integration was carried out using SAINT+[69]. Scaling and empirical absorption corrections were then applied using TWINABS.[69] The structure was solved as above using a HKLF 5 command with a resulting BASF parameter of 0.318.

[Yb(ttfpz)$_2$(dme)$_2$] (7):

Thiophene group S(2) was disordered over two positions, its occupancy was freely refined to be 80:20. The disordered part of that disorder was restrained using DFIX and DANG commands. Atoms C(13A), C(14A) and C(15A) were restrained using SIMU. Dme-oxygen atom O(3) and neighbouring C-atoms were disordered over two positions, their occupancy was freely refined to be appr. 55:45.

Also, DFIX was used to restraint the distance between C(23A) and O(4). EADP C6 C5 was also applied.

[Ba(ttfpz)$_2$(dme)$_3$] (8):

Thiophene groups were disordered over two positions, their occupancies were freely refined against each other. Their occupancies were refined to be 64:36 for S(2), 73:27 for S(3) and 74:26 for S(4). All disordered parts were restrained using DFIX, DANG and FLAT restraints. SIMU restraints were placed on thiophene groups S(2), S(3), S(3A), S(4) and S(4A).