Supplementary Material

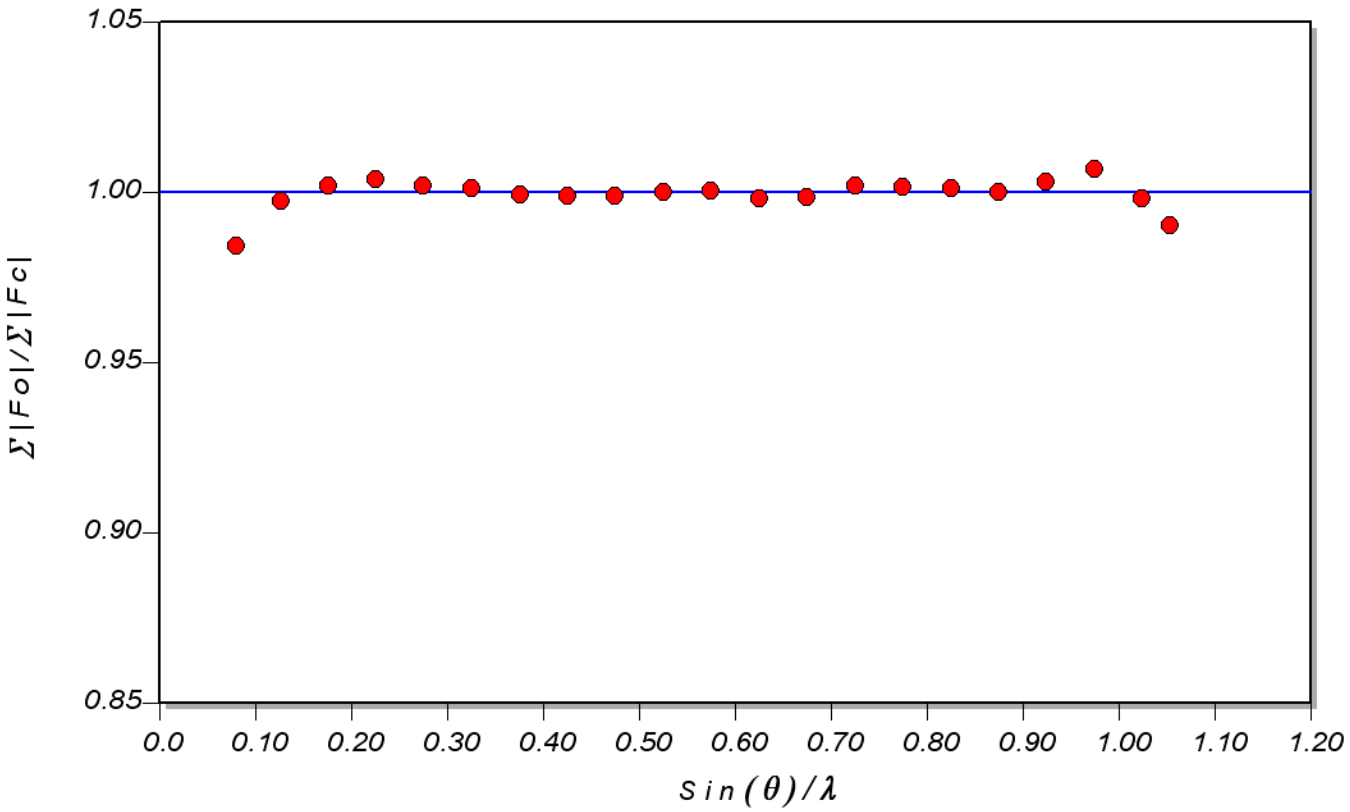

Figure S1 - *Plot of* $\Sigma|F_o|/\Sigma|F_c|$ *versus* $\sin\theta/\lambda$ for **[1–Cy][HCB$_{11}$Me$_{11}$]** after the multipole refinement.

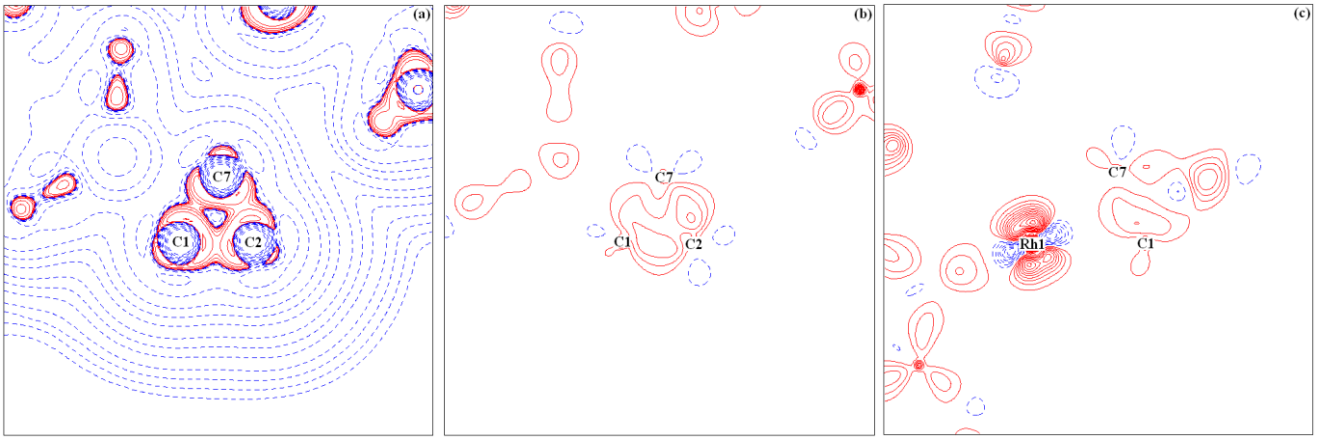

Figure S2. (a) Negative Laplacian of the electron density for **[1–Cy][HCB$_{11}$Me$_{11}$]** drawn in the plane C1-C2-C7. Positive contours are solid red lines, negative contours are dashed blue lines. (b) Deformation density map for **[1–Cy][HCB$_{11}$Me$_{11}$]** drawn in the plane C1-C2-C7. Positive contours are solid red lines, negative contours are dashed blue lines, the zero line is omitted. Contours are depicted at the 0.1 e Å^{-3}. (c) Deformation density map for **[1–Cy][HCB$_{11}$Me$_{11}$]**, drawn in the plane of Rh1-C1-C7. Contours are depicted at the 0.1 e Å^{-3}. Positive contours are solid red lines, negative contours are dashed blue lines. The zero line is omitted.

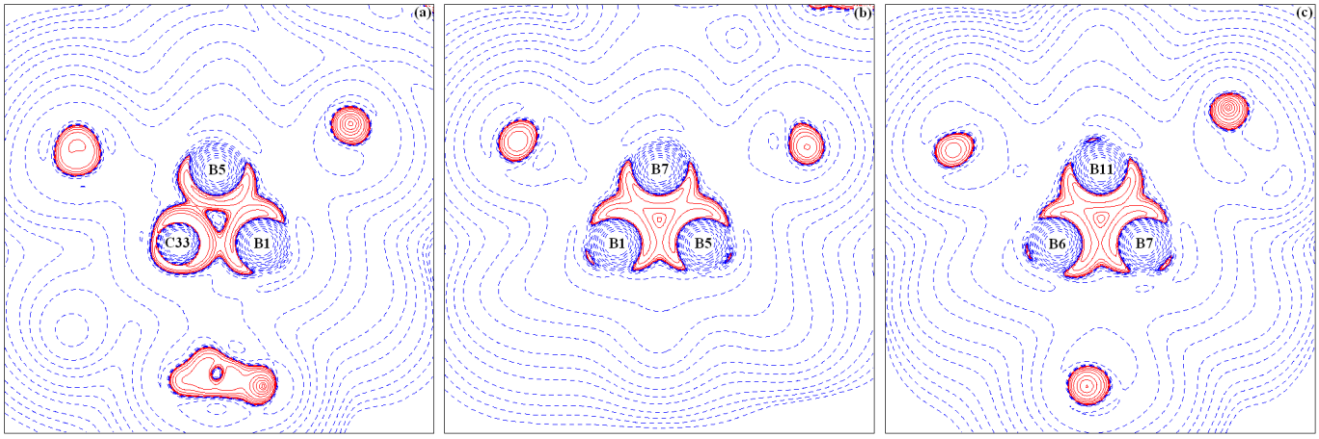

Figure S3. Negative Laplacian of the electron density for **[1–Cy][HCB$_{11}$Me$_{11}$]**. Positive contours are solid red lines, negative contours are dashed blue lines. Drawn in the plane (a) B1-B5-C33, (b) B1-B5-B7, (c) B6-B7-B11.

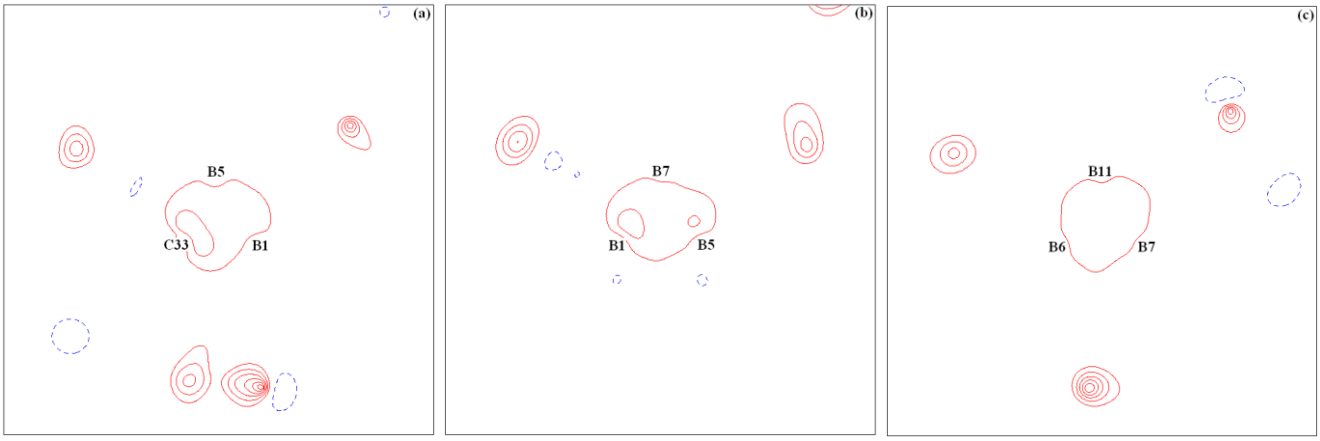

Figure S4. Deformation density map for **[1–Cy][HCB$_{11}$Me$_{11}$]**. Positive contours are solid red lines, negative contours are dashed blue lines, the zero line is omitted. Contours are depicted at the 0.1 e Å^{-3}. Drawn in the plane (a) B1-B5-C33, (b) B1-B5-B7, (c) B6-B7-B11.

Table S1 - *Hirshfeld analysis for* ***[1–Cy][HCB$_{11}$Me$_{11}$]***.

Atoms	DMSDA
Rh1-C1	31
Rh1-C7	30
Rh1-C9	17
Rh1-C14	16
Rh1-P1	4
P1-C15	7
P1-C21	7
P1-C27	11
C1-C2	5
C1-C5	-1
C1-C7	5
C2-C3	-1
C2-C7	4
C3-C4	-5
C4-C5	3
C4-C6	-4
C5-C8	-1
C6-C7	-3
C6-C13	-1
C8-C9	1
C8-C12	-1
C9-C10	1
C10-C11	3
C10-C14	4
C11-C12	-4
C12-C13	-2
C13-C14	-5
C15-C16	1
C15-C20	2
C16-C17	0
C17-C18	-1
C18-C19	-3
C19-C20	-4
C21-C22	-1
C21-C26	-3
C22-C23	0
C23-C24	-2
C24-C25	3
C25-C26	-1
C27-C28	1
C27-C32	-1
C28-C29	3
C29-C30	-2
C30-C31	2
C31-C32	-3

Atoms	DMSDA
B1-B2	0
B1-B5	0
B1-B7	2
B1-B8	1
B1-C33	-2
B1-C34	-9
B2-B3	-1
B2-B8	-2
B2-B9	-5
B2-C33	7
B2-C35	-7
B3-B4	-2
B3-B9	0
B3-B10	3
B3-C33	-9
B3-C36	-9
B4-B5	-3
B4-B6	-3
B4-B10	1
B4-C33	0
B4-C37	-10
B5-B6	1
B5-B7	-2
B5-C33	6
B5-C38	-10
B6-B7	3
B6-B10	-3
B6-B11	1
B6-C39	-7
B7-B8	-1
B7-B11	0
B7-C40	-10
B8-B9	2
B8-B11	4
B8-C41	-11
B9-B10	0
B9-B11	4
B9-C42	-11
B10-B11	5
B10-C43	-6
B11-C44	-5