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Supplementary Information

# Structure-property relationships of aromatic polyamides and polythioamides: comparative consideration with those of analogous polyesters, polythioesters and polydithioesters

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**Appendix A** Statistical Weight Matrices $U_j$'s ($j$, bond number) of PA2T ans PTA2T

For the bond numbers, see Fig. 2. Here, the symbol $\otimes$ stands for direct product.

$$U_1 = C_1 \otimes R_3 \tag{A1}$$

$$U_2 = C_3 \otimes R_1 \tag{A2}$$

$$U_3 = C_1 \otimes R_\gamma \tag{A3}$$

$$U_4 = C_6 \otimes R_1 \tag{A4}$$

$$U_5 = C_1 \otimes R_3 \tag{A5}$$

$$U_6 = I_3 \otimes R_3 \tag{A6}$$

$$U_7 = U_\mathrm{f} = \begin{bmatrix} \sigma_{\mathrm{ttt}} & \sigma_{\mathrm{tttg+}} & \sigma_{\mathrm{ttg-}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \sigma_{\mathrm{tg+t}} & \sigma_{\mathrm{tg+g+}} & \sigma_{\mathrm{tg+g-}} & 0 & 0 & \\ 0 & 0 & 0 & 0 & 0 & 0 & \sigma_{\mathrm{tg-t}} & \sigma_{\mathrm{tg-g+}} & \sigma_{\mathrm{tg-g-}} \\ \sigma_{\mathrm{g+tt}} & \sigma_{\mathrm{g+tg+}} & \sigma_{\mathrm{g+tg-}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \sigma_{\mathrm{g+g+t}} & \sigma_{\mathrm{g+g+g+}} & \sigma_{\mathrm{g+g+g-}} & 0 & 0 & \\ 0 & 0 & 0 & 0 & 0 & 0 & \sigma_{\mathrm{g+g-t}} & \sigma_{\mathrm{g+g-g+}} & \sigma_{\mathrm{g+g-g-}} \\ \sigma_{\mathrm{g-tt}} & \sigma_{\mathrm{g-tg+}} & \sigma_{\mathrm{g-tg-}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \sigma_{\mathrm{g-g+t}} & \sigma_{\mathrm{g-g+g+}} & \sigma_{\mathrm{g-g+g-}} & 0 & 0 & \\ 0 & 0 & 0 & 0 & 0 & 0 & \sigma_{\mathrm{g-g-t}} & \sigma_{\mathrm{g-g-g+}} & \sigma_{\mathrm{g-g-g-}} \end{bmatrix} \tag{A7}$$

$$U_\mathrm{a} = C_3 \otimes I_3 \otimes R_1 \tag{A8}$$

$$U_\mathrm{b} = C_3 \otimes S_1 \otimes R_\gamma \tag{A9}$$

$$U_\mathrm{c} = C_1 \otimes I_6 \otimes R_1 \tag{A10}$$

$$U_\mathrm{d} = C_6 \otimes S_1 \otimes R_3 \tag{A11}$$

$$U_\mathrm{e} = C_1 \otimes I_3 \otimes R_3 \tag{A12}$$

and

$$U_\mathrm{n} = C_3 \otimes I_3 \otimes R_1 \tag{A13}$$

where

$$C_1 = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \tag{A14}$$

$$C_3 = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \tag{A15}$$

$$C_6 = \begin{bmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{bmatrix} \tag{A16}$$

$$R_1 = \begin{bmatrix} 1 & 0 & 0 \end{bmatrix} \tag{A17}$$

$$R_3 = \begin{bmatrix} 1 & 1 & 1 \end{bmatrix} \tag{A18}$$

$$R_\gamma = \begin{bmatrix} \gamma_{\text{t–t}} & \gamma_{\text{(t–c)}^+} & \gamma_{\text{(t–c)}^-} & \gamma_{\text{(c–t)}^+} & \gamma_{\text{(c–t)}^-} & \gamma_{\text{c–c}} \end{bmatrix} \tag{A19}$$

$$S_1 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{A20}$$

and $I_3$ and $I_6$ are the identity matrices of sizes 3 and 6 respectively, with $\gamma_\xi = \exp(-\Delta G_\xi / RT)$ ($\xi$: orientation around bond 3 or b) and $\sigma_k = \exp(-\Delta G_k / RT)$ ($k$: conformations in bonds 5, 6, and 7 or bonds d, e, and f).

**Appendix B** Statistical Weight Matrices $U_j$'s ($j$, bond number) of PA3T ans PTA3T

The $U_1$ to $U_6$ matrices are the same as those of PA2T ans PTA2T.

$$U_7 = I_3 \otimes I_3 \otimes R_3 \tag{A21}$$

$$U_\text{a} = C_3 \otimes I_3 \otimes I_3 \otimes R_1 \tag{A22}$$

$$U_\text{b} = C_3 \otimes I_3 \otimes S_1 \otimes R_\gamma \tag{A23}$$

$$U_\text{c} = C_1 \otimes S_1 \otimes I_6 \otimes R_1 \tag{A24}$$

$$U_\text{d} = C_1 \otimes I_6 \otimes S_1 \otimes R_3 \tag{A25}$$

$$U_\text{e} = C_6 \otimes S_1 \otimes I_3 \otimes R_3 \tag{A26}$$

$$U_\text{f} = C_1 \otimes I_3 \otimes I_3 \otimes R_3 \tag{A27}$$

and

$$U_\text{n} = C_3 \otimes I_3 \otimes I_3 \otimes R_1 \tag{A28}$$

The $U_8$ and $U_\text{g}$ matrices are defined on the next page.

$$
U_8 = U_g =
\begin{array}{c|cccccccccccccccccccccccccc}
5\ 6\ 7 \mid 8 & t & g^+ & g^- & t & g^+ & g^- & t & g^+ & g^- & t & g^+ & g^- & t & g^+ & g^- & t & g^+ & g^- & t & g^+ & g^- & t & g^+ & g^- & t & g^+ & g^- \\
\hline
t\ t\ t & \sigma & \sigma & \sigma & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
t\ t\ g^+ & 0 & 0 & 0 & \sigma & \sigma & \sigma & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
t\ t\ g^- & 0 & 0 & 0 & 0 & 0 & 0 & \sigma & \sigma & \sigma & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
t\ g^+t & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sigma & \sigma & \sigma & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
t\ g^+g^+ & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sigma & \sigma & \sigma & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
t\ g^+g^- & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sigma & \sigma & \sigma & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
t\ g^-t & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sigma & \sigma & \sigma & 0 & 0 & 0 & 0 & 0 & 0 \\
t\ g^-g^+ & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sigma & \sigma & \sigma & 0 & 0 & 0 \\
t\ g^-g^- & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sigma & \sigma & \sigma \\
g^+t\ t & \sigma & \sigma & \sigma & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
g^+t\ g^+ & 0 & 0 & 0 & \sigma & \sigma & \sigma & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
g^+t\ g^- & 0 & 0 & 0 & 0 & 0 & 0 & \sigma & \sigma & \sigma & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
g^+g^+t & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sigma & \sigma & \sigma & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
g^+g^+g^+ & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sigma & \sigma & \sigma & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
g^+g^+g^- & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sigma & \sigma & \sigma & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
g^+g^-t & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sigma & \sigma & \sigma & 0 & 0 & 0 & 0 & 0 & 0 \\
g^+g^-g^+ & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sigma & \sigma & \sigma & 0 & 0 & 0 \\
g^+g^-g^- & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sigma & \sigma & \sigma \\
g^-t\ t & \sigma & \sigma & \sigma & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
g^-t\ g^+ & 0 & 0 & 0 & \sigma & \sigma & \sigma & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
g^-t\ g^- & 0 & 0 & 0 & 0 & 0 & 0 & \sigma & \sigma & \sigma & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
g^-g^+t & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sigma & \sigma & \sigma & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
g^-g^+g^+ & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sigma & \sigma & \sigma & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
g^-g^+g^- & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sigma & \sigma & \sigma & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
g^-g^-t & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sigma & \sigma & \sigma & 0 & 0 & 0 & 0 & 0 & 0 \\
g^-g^-g^+ & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sigma & \sigma & \sigma & 0 & 0 & 0 \\
g^-g^-g^- & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sigma & \sigma & \sigma
\end{array}
\tag{A29}
$$

where each $\sigma$ is the Boltzmann factor for the Gibbs free energy of the conformation expressed on the left (bonds 5, 6, and 7 or bonds d, e, and f) and upper (bond 8 or g) ends of the matrix. For example, the (6, 16) element corresponds to $\sigma_{\mathrm{tg+g-t}} = \exp(\Delta G_{\mathrm{tg+g-t}}/RT)$.

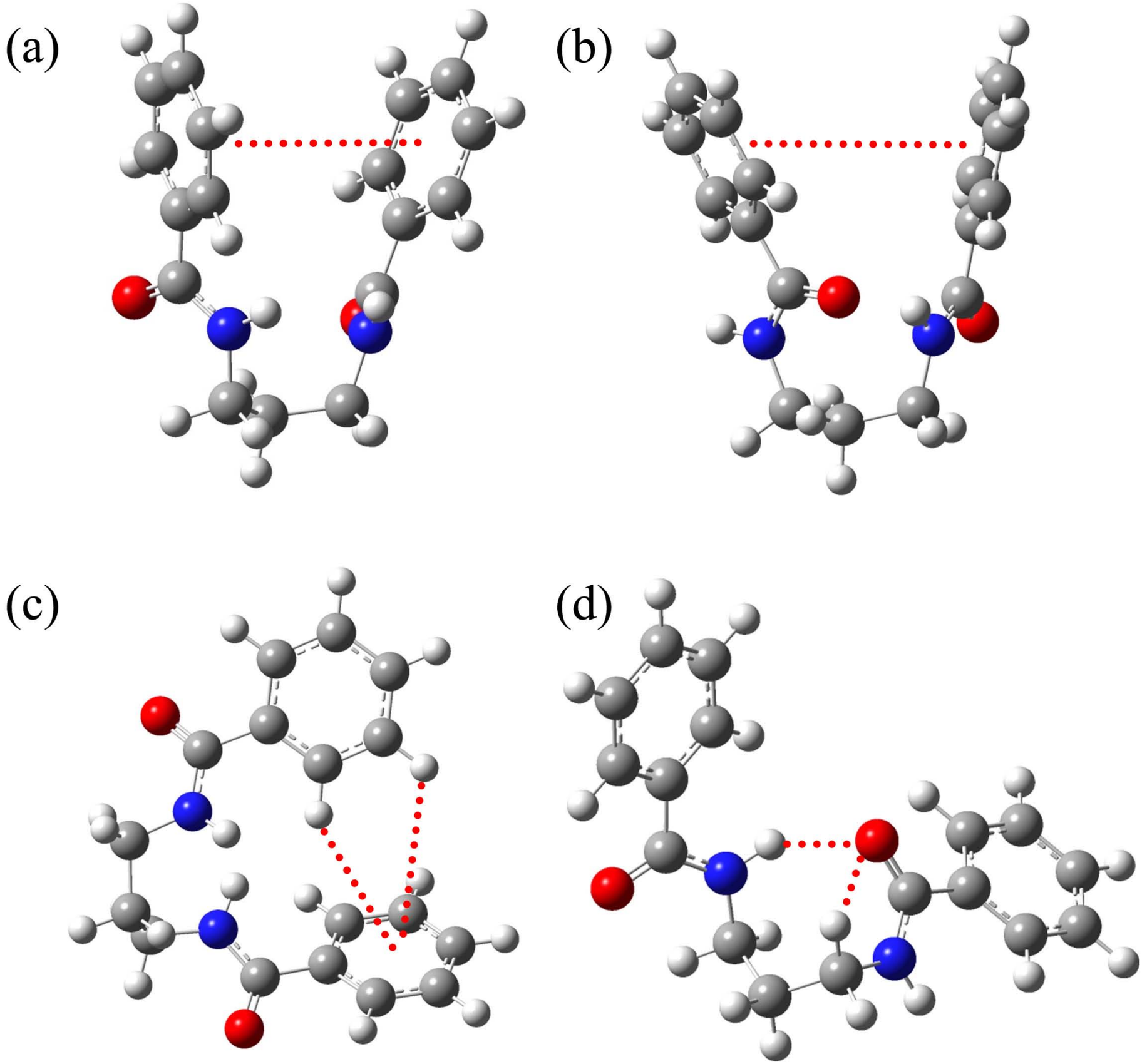


**Fig. S1** Intramolecular interactions of 3DBA: π/π of (a) g+g+g-g- and (b) g+g+g-g+; C-H...π of (c) tg+g-g-; NH...O=C of g+g+g+g-.

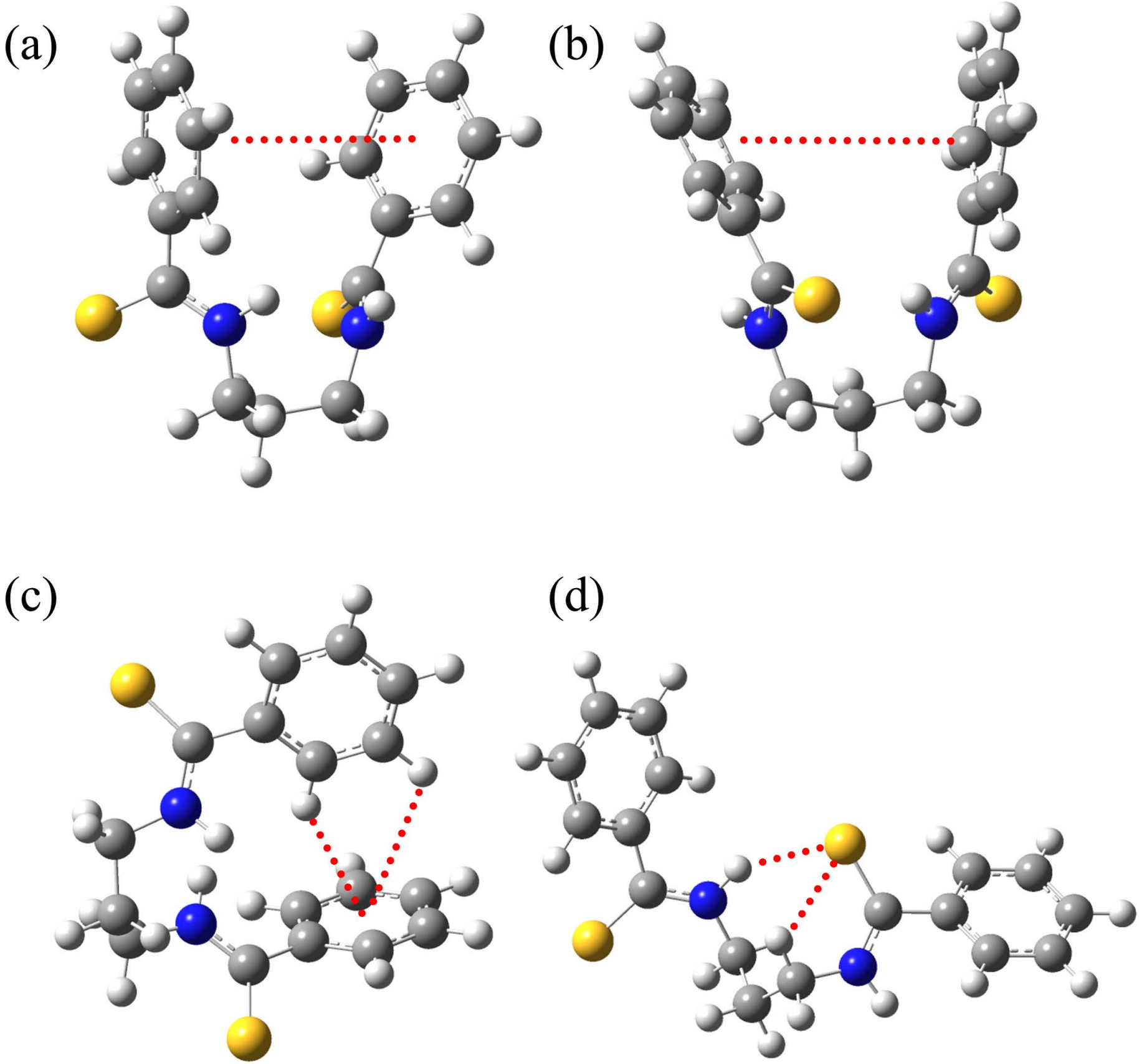


**Fig. S2** Intramolecular interactions of 3DBTA: π/π of (a) g+g+g-g- and (b) g+g+g-g+; C-H...π of (c) tg+g-g-; NH..S=C of g+g+g+g-.

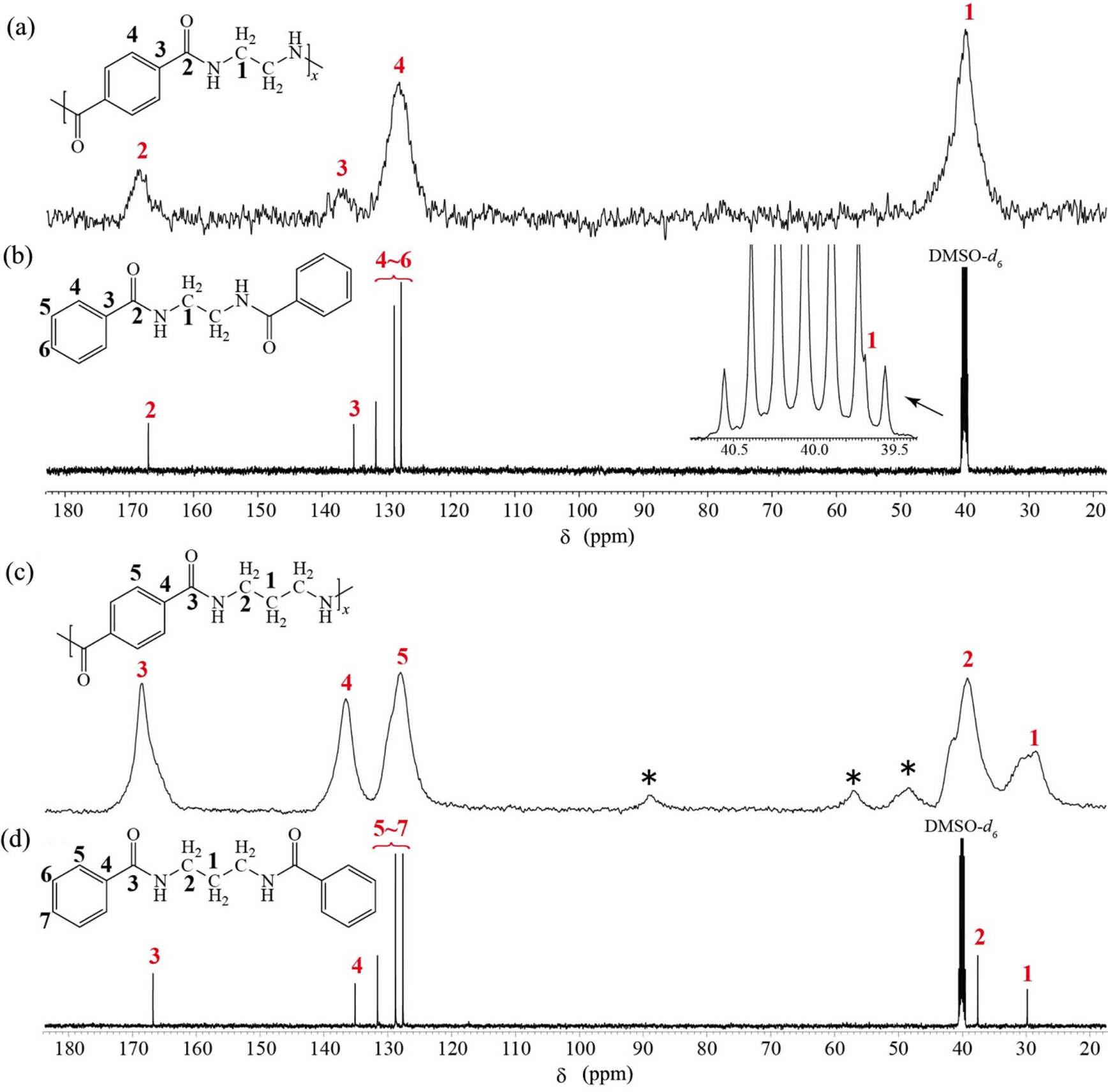


**Fig. S3** Solid-state $^{13}$C NMR spectra observed from (a) PA2T and (c) PA3T, compared with solution spectra from (b) 2DBA and (d) 3DBA dissolved in DMSO-$d_6$. The peaks were assigned as indicated, and the asterisk represents the spinning sideband.

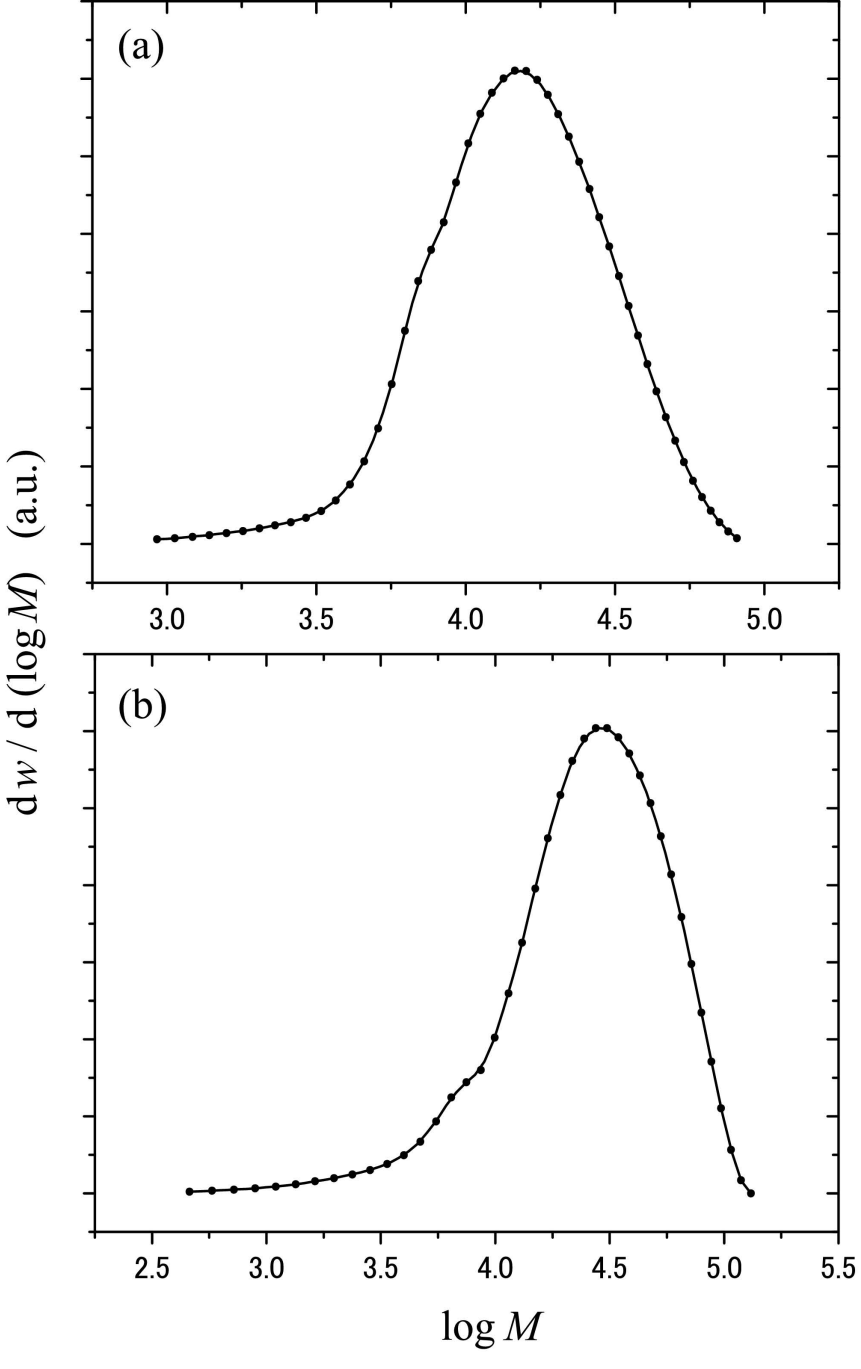


**Fig. S4** Molecular weight distributions of (a) PTA2T and (b) PTA3T.

**Table S1** Geometrical parameters of PA2T, used in the refined RIS calculations

| conformation | | | | | | |
|---|---|---|---|---|---|---|
| | bond[a] | | | | | |
| $j-1$ | $j$ | $j+1$ | $l_j$ [b] | $\theta_{j-1}$ [c] | $\theta_j$ [d] | $\phi_j$ [e] |
| | | | bond a (c) | | | |
| t | t | t-t | 1.352 | 121.5 | 116.8 | 1.5 |
| $g^+$ | | | 1.362 | 122.3 | 117.8 | −1.9 |
| $g^-$ | | | 1.362 | 122.3 | 117.8 | 1.9 |
| t | t | $(t\text{-}c)^+$ | 1.352 | 121.5 | 116.7 | 0.3 |
| $g^+$ | | | 1.361 | 122.4 | 117.9 | −0.7 |
| $g^-$ | | | 1.361 | 122.4 | 117.9 | −0.7 |
| t | t | $(t\text{-}c)^-$ | 1.352 | 121.5 | 116.7 | −0.3 |
| $g^+$ | | | 1.361 | 122.4 | 117.9 | 0.7 |
| $g^-$ | | | 1.361 | 122.4 | 117.9 | 0.7 |
| t | t | $(c\text{-}t)^+$ | | | | |
| $g^+$ | | | 1.361 | 122.4 | 119.1 | 0.2 |
| $g^-$ | | | 1.361 | 122.4 | 119.1 | 0.2 |
| t | t | $(c\text{-}t)^-$ | | | | |
| $g^+$ | | | 1.361 | 122.4 | 119.1 | −0.2 |
| $g^-$ | | | 1.361 | 122.4 | 119.1 | −0.2 |
| t | t | c-c | 1.352 | 121.5 | 116.7 | 1.0 |
| $g^+$ | | | 1.362 | 122.3 | 119.1 | −2.3 |
| $g^-$ | | | 1.362 | 122.3 | 119.1 | 2.3 |
| | | | bond b | | | |
| t | t-t | t | 5.811 | 116.8 | 116.8 | 0.0 |
| | $(t\text{-}c)^+$ | | 5.811 | 116.7 | 116.7 | 53.6 |
| | $(t\text{-}c)^-$ | | 5.811 | 116.7 | 116.7 | −53.6 |
| | $(c\text{-}t)^+$ | | 5.809 | 116.8 | 116.8 | 123.0 |
| | $(c\text{-}t)^-$ | | 5.809 | 116.8 | 116.8 | −123.0 |
| | c-c | | 5.809 | 116.7 | 116.7 | 180.0 |
| | | | bond d (f) | | | |
| t | t | t | | | | |
| | $g^+$ | | 1.453 | 123.2 | 112.3 | 87.7 |
| | $g^-$ | | 1.453 | 123.2 | 112.3 | −87.7 |
| | t | $g^+$ | 1.457 | 122.1 | 111.1 | 3.3 |
| | $g^+$ | | 1.456 | 122.9 | 113.7 | 94.1 |
| | $g^-$ | | 1.462 | 123.2 | 114.6 | −93.8 |
| | t | $g^-$ | 1.457 | 122.1 | 111.1 | −3.3 |
| | $g^+$ | | 1.462 | 123.2 | 114.6 | 93.8 |
| | $g^-$ | | 1.456 | 122.9 | 113.7 | −94.1 |
| | | | bond e | | | |
| t | t | t | | | | |
| | $g^+$ | | | | | |
| | $g^-$ | | | | | |
| $g^+$ | t | | | | | |
| | $g^+$ | | | | | |
| | $g^-$ | | 1.525 | | 111.1 | −112.7 |
| $g^-$ | t | | | | | |
| | $g^+$ | | 1.525 | | 111.1 | 112.7 |
| | $g^-$ | | | | | |
| t | t | $g^+$ | | | | |
| | $g^+$ | | | | | |
| | $g^-$ | | 1.525 | | 114.6 | −112.7 |
| $g^+$ | t | | 1.538 | | 112.3 | 2.5 |
| | $g^+$ | | 1.534 | | 113.7 | 116.8 |
| | $g^-$ | | 1.532 | | 113.6 | −119.0 |
| $g^-$ | t | | 1.538 | | 112.1 | 0.5 |
| | $g^+$ | | 1.533 | | 113.7 | 116.7 |
| | $g^-$ | | 1.533 | | 113.0 | −116.7 |
| t | t | $g^-$ | | | | |
| | $g^+$ | | 1.525 | | 114.6 | 112.7 |
| | $g^-$ | | | | | |
| $g^+$ | t | | 1.538 | | 112.1 | 0.5 |
| | $g^+$ | | 1.533 | | 113.0 | 116.7 |
| | $g^-$ | | 1.533 | | 113.7 | −116.7 |
| $g^-$ | t | | 1.538 | | 112.3 | −2.5 |
| | $g^+$ | | 1.532 | | 113.6 | 119.0 |
| | $g^-$ | | 1.534 | | 113.7 | −116.8 |

[a] $j$ denotes the current bond. The blank line represents that the conformation is inexistent. [b] Length of bond $j$ in Å. [c] Angle formed between bonds $j-1$ and $j$ in deg. [d] Angle formed between bonds $j$ and $j+1$ in deg. [e] Dihedral angle of bond $j$ in deg.

**Table S2** Geometrical parameters of PTA2T, used in the refined RIS calculations

| conformation | | | | | | |
|---|---|---|---|---|---|---|
| | bond[a] | | | | | |
| $j-1$ | $j$ | $j+1$ | $l_j$ [b] | $\theta_{j-1}$ [c] | $\theta_j$ [d] | $\phi_j$ [e] |
| | | | bond a (c) | | | |
| t | t | t-t | 1.336 | 124.3 | 115.4 | 1.8 |
| $g^+$ | | | 1.342 | 126.2 | 114.8 | 3.5 |
| $g^-$ | | | 1.342 | 126.2 | 114.8 | −3.5 |
| t | t | $(t\text{-}c)^+$ | 1.336 | 124.6 | 115.5 | 2.8 |
| $g^+$ | | | 1.341 | 126.4 | 114.4 | 3.0 |
| $g^-$ | | | 1.341 | 126.4 | 114.4 | 3.0 |
| | t | $(t\text{-}c)^-$ | 1.336 | 124.6 | 115.5 | −2.8 |
| $g^+$ | | | 1.341 | 126.4 | 114.4 | −3.0 |
| $g^-$ | | | 1.341 | 126.4 | 114.4 | −3.0 |
| t | t | $(c\text{-}t)^+$ | 1.335 | 124.6 | 115.6 | −2.4 |
| $g^+$ | | | 1.341 | 126.3 | 114.8 | −2.9 |
| $g^-$ | | | 1.341 | 126.3 | 114.8 | −2.9 |
| t | t | $(c\text{-}t)^-$ | 1.335 | 124.6 | 115.6 | 2.4 |
| $g^+$ | | | 1.341 | 126.3 | 114.8 | 2.9 |
| $g^-$ | | | 1.341 | 126.3 | 114.8 | 2.9 |
| t | t | c-c | 1.337 | 124.3 | 115.8 | 1.7 |
| $g^+$ | | | 1.342 | 126.2 | 114.9 | 3.7 |
| $g^-$ | | | 1.342 | 126.2 | 114.9 | −3.7 |
| | | | bond b | | | |
| t | t-t | t | 5.793 | 115.4 | 115.4 | 0.0 |
| | $(t\text{-}c)^+$ | | 5.794 | 115.5 | 115.5 | 79.6 |
| | $(t\text{-}c)^-$ | | 5.794 | 115.5 | 115.5 | −79.6 |
| | $(c\text{-}t)^+$ | | 5.792 | 115.6 | 115.6 | 98.0 |
| | $(c\text{-}t)^-$ | | 5.792 | 115.6 | 115.6 | −98.0 |
| | c-c | | 5.792 | 115.8 | 115.8 | 180.0 |
| | | | bond d (f) | | | |
| t | t | t | 1.456 | 125.3 | 109.7 | −9.3 |
| | $g^+$ | | 1.454 | 126.2 | 111.5 | 89.9 |
| | $g^-$ | | 1.454 | 126.2 | 111.5 | −89.9 |
| | t | $g^+$ | 1.458 | 124.6 | 111.8 | 0.2 |
| | $g^+$ | | 1.457 | 126.2 | 113.6 | 93.1 |
| | $g^-$ | | 1.461 | 126.8 | 114.2 | −81.8 |
| | t | $g^-$ | 1.458 | 124.6 | 111.8 | −0.2 |
| | $g^+$ | | 1.461 | 126.8 | 114.2 | 81.8 |
| | $g^-$ | | 1.457 | 126.2 | 113.6 | −93.1 |
| | | | bond e | | | |
| t | t | t | 1.526 | | 109.6 | 0.4 |
| | $g^+$ | | 1.520 | | 111.7 | 111.5 |
| | $g^-$ | | 1.520 | | 111.7 | −111.5 |
| $g^+$ | t | | 1.531 | | 109.7 | −1.5 |
| | $g^+$ | | 1.530 | | 112.1 | 113.8 |
| | $g^-$ | | 1.525 | | 111.8 | −112.1 |
| $g^-$ | t | | 1.531 | | 109.7 | 1.5 |
| | $g^+$ | | 1.525 | | 111.8 | 112.1 |
| | $g^-$ | | 1.530 | | 112.1 | −113.8 |
| t | t | $g^+$ | 1.531 | | 111.6 | −1.5 |
| | $g^+$ | | 1.530 | | 113.5 | 113.8 |
| | $g^-$ | | 1.525 | | 114.2 | −112.1 |
| $g^+$ | t | | 1.539 | | 111.6 | 9.8 |
| | $g^+$ | | 1.533 | | 113.6 | 116.8 |
| | $g^-$ | | | | | |
| $g^-$ | t | | 1.538 | | 111.5 | −0.7 |
| | $g^+$ | | | | | |
| | $g^-$ | | | | | |
| t | t | $g^-$ | 1.531 | | 111.6 | 1.5 |
| | $g^+$ | | 1.525 | | 114.2 | 112.1 |
| | $g^-$ | | 1.530 | | 113.5 | −113.8 |
| $g^+$ | t | | 1.538 | | 111.5 | 0.7 |
| | $g^+$ | | | | | |
| | $g^-$ | | | | | |
| $g^-$ | t | | 1.539 | | 111.6 | −9.8 |
| | $g^+$ | | | | | |
| | $g^-$ | | 1.533 | | 113.6 | −116.8 |

[a] $j$ denotes the current bond. The blank line represents that the conformation is inexistent. [b]Length of bond $j$ in Å. [c]Angle formed between bonds $j-1$ and $j$ in deg. [d]Angle formed between bonds $j$ and $j+1$ in deg. [e]Dihedral angle of bond $j$ in deg.

**Table S3** Geometrical parameters of PA3T, used in the refined RIS calculations

| conformation | | | | | | |
|---|---|---|---|---|---|---|
| | bond[a] | | | | | |
| $j-1$ | $j$ | $j+1$ | $l_j$ [b] | $\theta_{j-1}$ [c] | $\theta_j$ [d] | $\phi_j$ [e] |
| | | | bond a (c) | | | |
| t | t | t-t | | | | |
| $g^+$ | | | 1.360 | 123.4 | 117.6 | −0.6 |
| $g^-$ | | | 1.360 | 123.4 | 117.6 | 0.6 |
| t | t | $(t\text{-}c)^+$ | | | | |
| $g^+$ | | | 1.360 | 122.3 | 117.9 | −1.8 |
| $g^-$ | | | 1.360 | 122.3 | 117.9 | −1.8 |
| t | t | $(t\text{-}c)^-$ | | | | |
| $g^+$ | | | 1.360 | 122.3 | 117.9 | 1.8 |
| $g^-$ | | | 1.360 | 122.3 | 117.9 | 1.8 |
| t | t | $(c\text{-}t)^+$ | | | | |
| $g^+$ | | | 1.359 | 122.7 | 119.3 | −1.6 |
| $g^-$ | | | 1.359 | 122.7 | 119.3 | −1.6 |
| t | t | $(c\text{-}t)^-$ | | | | |
| $g^+$ | | | 1.359 | 122.7 | 119.3 | 1.6 |
| $g^-$ | | | 1.359 | 122.7 | 119.3 | 1.6 |
| t | t | c-c | | | | |
| $g^+$ | | | 1.359 | 122.8 | 119.1 | −1.6 |
| $g^-$ | | | 1.359 | 122.8 | 119.1 | 1.6 |
| | | | bond b | | | |
| t | t-t | t | 5.825 | 118.1 | 118.1 | 0.0 |
| | $(t\text{-}c)^+$ | | 5.824 | 118.0 | 118.0 | 46.9 |
| | $(t\text{-}c)^-$ | | 5.824 | 118.0 | 118.0 | −46.9 |
| | $(c\text{-}t)^+$ | | 5.823 | 119.4 | 119.4 | 129.2 |
| | $(c\text{-}t)^-$ | | 5.823 | 119.4 | 119.4 | −129.2 |
| | c-c | | 5.822 | 119.2 | 119.2 | 180.0 |
| | | | bond d (g) | | | |
| t | t | t | 1.458 | 122.6 | 110.9 | −19.0 |
| | $g^+$ | | 1.457 | 123.3 | 113.1 | 88.8 |
| | $g^-$ | | 1.457 | 123.3 | 113.1 | −88.8 |
| | t | $g^+$ | | | | |
| | $g^+$ | | 1.456 | 123.8 | 113.6 | 76.9 |
| | $g^-$ | | 1.461 | 123.5 | 113.3 | −34.8 |
| | t | $g^-$ | | | | |
| | $g^+$ | | 1.461 | 123.5 | 113.3 | 34.8 |
| | $g^-$ | | 1.456 | 123.8 | 113.6 | −76.9 |
| | | | bond e (f) | | | |
| t | t | t | 1.526 | 110.9 | 111.1 | −1.0 |
| | $g^+$ | | 1.530 | 112.6 | 113.1 | 113.1 |
| | $g^-$ | | 1.530 | 112.6 | 113.1 | −113.1 |
| $g^+$ | t | | 1.532 | 113.1 | 111.4 | 1.1 |
| | $g^+$ | | 1.532 | 114.0 | 113.2 | 114.1 |
| | $g^-$ | | 1.531 | 113.8 | 113.3 | −113.7 |
| $g^-$ | t | | 1.532 | 113.1 | 111.4 | −1.1 |
| | $g^+$ | | 1.531 | 113.8 | 113.3 | 113.7 |
| | $g^-$ | | 1.532 | 114.0 | 113.2 | −114.1 |
| t | t | $g^+$ | 1.527 | 111.1 | 113.3 | −2.0 |
| | $g^+$ | | 1.529 | 112.3 | 114.8 | 114.2 |
| | $g^-$ | | 1.528 | 113.2 | 115.7 | −109.4 |
| $g^+$ | t | | 1.532 | 112.7 | 113.2 | 0.5 |
| | $g^+$ | | 1.533 | 113.6 | 114.9 | 124.4 |
| | $g^-$ | | 1.528 | 113.3 | 115.7 | −113.3 |
| $g^-$ | t | | 1.532 | 113.0 | 113.0 | −2.6 |
| | $g^+$ | | 1.530 | 112.5 | 114.8 | 114.5 |
| | $g^-$ | | 1.534 | 115.1 | 115.7 | −105.4 |
| t | t | $g^-$ | 1.527 | 111.1 | 113.3 | 2.0 |
| | $g^+$ | | 1.528 | 113.2 | 115.7 | 109.4 |
| | $g^-$ | | 1.529 | 112.3 | 114.8 | −114.2 |
| $g^+$ | t | | 1.532 | 113.0 | 113.0 | 2.6 |
| | $g^+$ | | 1.534 | 115.1 | 115.7 | 105.4 |
| | $g^-$ | | 1.530 | 112.5 | 114.8 | −114.5 |
| $g^-$ | t | | 1.532 | 112.7 | 113.2 | −0.5 |
| | $g^+$ | | 1.528 | 113.3 | 115.7 | 113.3 |
| | $g^-$ | | 1.533 | 113.6 | 114.9 | −124.4 |

[a] $j$ denotes the current bond. The blank line represents that the conformation is inexistent. [b]Length of bond $j$ in Å. [c]Angle formed between bonds $j-1$ and $j$ in deg. [d]Angle formed between bonds $j$ and $j+1$ in deg. [e]Dihedral angle of bond $j$ in deg.

**Table S4** Geometrical parameters of PTA3T, used in the refined RIS calculations

| conformation | | | | | | |
|---|---|---|---|---|---|---|
| | bond[a] | | | | | |
| $j-1$ | $j$ | $j+1$ | $l_j$ [b] | $\theta_{j-1}$ [c] | $\theta_j$ [d] | $\phi_j$ [e] |
| | | | bond a (c) | | | |
| t | t | t-t | 1.338 | 125.3 | 115.1 | 2.4 |
| $g^+$ | | | 1.339 | 126.6 | 114.6 | 2.1 |
| $g^-$ | | | 1.339 | 126.6 | 114.6 | −2.1 |
| t | t | $(t\text{-}c)^+$ | 1.338 | 125.3 | 115.2 | 2.5 |
| $g^+$ | | | 1.339 | 126.6 | 114.5 | 3.9 |
| $g^-$ | | | 1.339 | 126.6 | 114.5 | 3.9 |
| t | t | $(t\text{-}c)^-$ | 1.338 | 125.3 | 115.2 | −2.5 |
| $g^+$ | | | 1.339 | 126.6 | 114.5 | −3.9 |
| $g^-$ | | | 1.339 | 126.6 | 114.5 | −3.9 |
| t | t | $(c\text{-}t)^+$ | 1.338 | 125.3 | 115.3 | −2.0 |
| $g^+$ | | | 1.339 | 126.6 | 114.6 | −1.8 |
| $g^-$ | | | 1.339 | 126.6 | 114.6 | −1.8 |
| t | t | $(c\text{-}t)^-$ | 1.338 | 125.3 | 115.3 | 2.0 |
| $g^+$ | | | 1.339 | 126.6 | 114.6 | 1.8 |
| $g^-$ | | | 1.339 | 126.6 | 114.6 | 1.8 |
| t | t | c-c | 1.338 | 125.4 | 115.1 | 2.2 |
| $g^+$ | | | 1.339 | 126.6 | 114.5 | 1.7 |
| $g^-$ | | | 1.339 | 126.6 | 114.5 | −1.7 |
| | | | bond b | | | |
| t | t-t | t | 5.809 | 115.1 | 115.1 | 0.0 |
| | $(t\text{-}c)^+$ | | 5.809 | 115.2 | 115.2 | 75.8 |
| | $(t\text{-}c)^-$ | | 5.809 | 115.2 | 115.2 | −75.8 |
| | $(c\text{-}t)^+$ | | 5.808 | 115.3 | 115.3 | 102.5 |
| | $(c\text{-}t)^-$ | | 5.808 | 115.3 | 115.3 | −102.5 |
| | c-c | | 5.808 | 115.1 | 115.1 | 180.0 |
| | | | bond d (g) | | | |
| t | t | t | 1.458 | 125.4 | 110.5 | 6.2 |
| | $g^+$ | | 1.458 | 126.4 | 112.3 | 88.9 |
| | $g^-$ | | 1.458 | 126.4 | 112.3 | −88.9 |
| | t | $g^+$ | 1.461 | 125.6 | 111.6 | −9.9 |
| | $g^+$ | | 1.461 | 126.1 | 114.0 | 112.7 |
| | $g^-$ | | 1.460 | 127.4 | 112.5 | −59.0 |
| | t | $g^-$ | 1.461 | 125.6 | 111.6 | 9.9 |
| | $g^+$ | | 1.460 | 127.4 | 112.5 | 59.0 |
| | $g^-$ | | 1.461 | 126.1 | 114.0 | −112.7 |
| | | | bond e (f) | | | |
| t | t | t | 1.525 | 110.5 | 110.7 | −0.6 |
| | $g^+$ | | 1.525 | 111.6 | 113.1 | 109.8 |
| | $g^-$ | | 1.525 | 111.6 | 113.1 | −109.8 |
| $g^+$ | t | | 1.532 | 112.6 | 110.8 | −0.3 |
| | $g^+$ | | 1.532 | 114.0 | 113.1 | 112.7 |
| | $g^-$ | | 1.530 | 112.5 | 113.0 | −113.0 |
| $g^-$ | t | | 1.532 | 112.6 | 110.8 | 0.3 |
| | $g^+$ | | 1.530 | 112.5 | 113.0 | 113.0 |
| | $g^-$ | | 1.532 | 114.0 | 113.1 | −112.7 |
| t | t | $g^+$ | 1.528 | 110.4 | 113.1 | 0.4 |
| | $g^+$ | | 1.528 | 111.4 | 115.1 | 110.7 |
| | $g^-$ | | 1.535 | 113.4 | 116.1 | −91.1 |
| $g^+$ | t | | 1.535 | 112.3 | 113.0 | −8.2 |
| | $g^+$ | | 1.534 | 113.8 | 115.3 | 115.2 |
| | $g^-$ | | 1.535 | 113.4 | 116.1 | −91.1 |
| $g^-$ | t | | 1.533 | 112.4 | 113.2 | −1.0 |
| | $g^+$ | | | | | |
| | $g^-$ | | 1.533 | 115.3 | 116.0 | −110.4 |
| t | t | $g^-$ | 1.528 | 110.4 | 113.1 | −0.4 |
| | $g^+$ | | 1.535 | 113.4 | 116.1 | 91.1 |
| | $g^-$ | | 1.528 | 111.4 | 115.1 | −110.7 |
| $g^+$ | t | | 1.533 | 112.4 | 113.2 | 1.0 |
| | $g^+$ | | 1.533 | 115.3 | 116.0 | 110.4 |
| | $g^-$ | | | | | |
| $g^-$ | t | | 1.535 | 112.3 | 113.0 | 8.2 |
| | $g^+$ | | 1.535 | 113.4 | 116.1 | 91.1 |
| | $g^-$ | | 1.534 | 113.8 | 115.3 | −115.2 |

[a] $j$ denotes the current bond. The blank line represents that the conformation is inexistent. [b] Length of bond $j$ in Å. [c] Angle formed between bonds $j-1$ and $j$ in deg. [d] Angle formed between bonds $j$ and $j+1$ in deg. [e] Dihedral angle of bond $j$ in deg.

**Table S5** Geometrical parameters of $P3TS_2$, used in the refined RIS calculations

| conformation | | | | | | |
|---|---|---|---|---|---|---|
| | bond[a] | | | | | |
| $j-1$ | $j$ | $j+1$ | $l_j$ [b] | $\theta_{j-1}$ [c] | $\theta_j$ [d] | $\phi_j$ [e] |
| | | | bond a (c) | | | |
| t | t | trans | 1.807 | 98.4 | 117.9 | 0.0 |
| $g^+$ | | | 1.809 | 99.0 | 117.7 | 0.2 |
| $g^-$ | | | 1.809 | 99.0 | 117.7 | −0.2 |
| t | t | cis | 1.808 | 98.5 | 118.8 | 0.0 |
| $g^+$ | | | 1.804 | 99.6 | 118.6 | −0.1 |
| $g^-$ | | | 1.804 | 99.6 | 118.6 | 0.1 |
| | | | bond b | | | |
| t | trans | t | 5.798 | 117.9 | 117.9 | 0.0 |
| | cis | | 5.787 | 118.8 | 118.8 | 180.0 |
| | | | bond d (g) | | | |
| t | t | t | 1.838 | 98.4 | 109.7 | 0.0 |
| | $g^+$ | | 1.835 | 98.9 | 113.5 | 97.4 |
| | $g^-$ | | 1.835 | 98.9 | 113.5 | −97.4 |
| | t | $g^+$ | 1.841 | 98.6 | 111.4 | −12.6 |
| | $g^+$ | | 1.838 | 98.7 | 114.7 | 96.9 |
| | $g^-$ | | 1.838 | 100.0 | 115.1 | −81.1 |
| | t | $g^-$ | 1.841 | 98.6 | 111.4 | 12.6 |
| | $g^+$ | | 1.838 | 100.0 | 115.1 | 81.1 |
| | $g^-$ | | 1.838 | 98.7 | 114.7 | −96.9 |
| | | | bond e (f) | | | |
| t | t | t | 1.532 | 109.7 | 110.3 | 0.0 |
| | $g^+$ | | 1.534 | 111.4 | 113.3 | 111.8 |
| | $g^-$ | | 1.534 | 111.4 | 113.3 | −111.8 |
| $g^+$ | t | | 1.532 | 113.5 | 110.5 | −1.6 |
| | $g^+$ | | 1.533 | 114.7 | 113.1 | 113.4 |
| | $g^-$ | | 1.535 | 115.1 | 113.6 | −114.2 |
| $g^-$ | t | | 1.532 | 113.5 | 110.5 | 1.6 |
| | $g^+$ | | 1.535 | 115.1 | 113.6 | 114.2 |
| | $g^-$ | | 1.533 | 114.7 | 113.1 | −113.4 |
| t | t | $g^+$ | 1.530 | 109.6 | 113.1 | −0.1 |
| | $g^+$ | | 1.532 | 111.0 | 116.0 | 114.2 |
| | $g^-$ | | 1.533 | 115.9 | 116.5 | −92.7 |
| $g^+$ | t | | 1.528 | 113.6 | 113.4 | 6.2 |
| | $g^+$ | | 1.533 | 114.0 | 115.2 | 107.4 |
| | $g^-$ | | 1.534 | 117.1 | 116.8 | −105.2 |
| $g^-$ | t | | 1.530 | 113.3 | 113.2 | −0.3 |
| | $g^+$ | | 1.533 | 114.0 | 115.2 | 107.4 |
| | $g^-$ | | 1.536 | 116.1 | 116.8 | −96.4 |
| t | t | $g^-$ | 1.530 | 109.6 | 113.1 | 0.1 |
| | $g^+$ | | 1.533 | 115.9 | 116.5 | 92.7 |
| | $g^-$ | | 1.532 | 111.0 | 116.0 | −114.2 |
| $g^+$ | t | | 1.530 | 113.3 | 113.2 | 0.3 |
| | $g^+$ | | 1.536 | 116.1 | 116.8 | 96.4 |
| | $g^-$ | | 1.533 | 114.0 | 115.2 | −107.4 |
| $g^-$ | t | | 1.528 | 113.6 | 113.4 | −6.2 |
| | $g^+$ | | 1.534 | 117.1 | 116.8 | 105.2 |
| | $g^-$ | | 1.533 | 114.0 | 115.2 | −107.4 |

[a] $j$ denotes the current bond. The blank line represents that the conformation is inexistent. [b]Length of bond $j$ in Å. [c]Angle formed between bonds $j-1$ and $j$ in deg. [d]Angle formed between bonds $j$ and $j+1$ in deg. [e]Dihedral angle of bond $j$ in deg.

**Table S6** Geometrical parameters of $P3TS_4$, used in the refined RIS calculations

| conformation | | | | | | |
|---|---|---|---|---|---|---|
| | bond[a] | | | | | |
| $j-1$ | $j$ | $j+1$ | $l_j$ [b] | $\theta_{j-1}$ [c] | $\theta_j$ [d] | $\phi_j$ [e] |
| | | | bond a (c) | | | |
| t | t | t-t | 1.758 | 103.9 | 113.0 | 3.1 |
| $g^+$ | | | 1.770 | 104.7 | 112.7 | 2.1 |
| $g^-$ | | | 1.770 | 104.7 | 112.7 | −2.1 |
| t | t | $(t\text{-}c)^+$ | 1.759 | 103.9 | 113.2 | 4.0 |
| $g^+$ | | | 1.772 | 104.2 | 112.1 | 5.9 |
| $g^-$ | | | 1.772 | 104.2 | 112.1 | 5.9 |
| t | t | $(t\text{-}c)^-$ | 1.759 | 103.9 | 113.2 | −4.0 |
| $g^+$ | | | 1.772 | 104.2 | 112.1 | −5.9 |
| $g^-$ | | | 1.772 | 104.2 | 112.1 | −5.9 |
| t | t | $(c\text{-}t)^+$ | 1.758 | 103.9 | 113.4 | −3.1 |
| $g^+$ | | | 1.771 | 104.7 | 113.0 | −5.5 |
| $g^-$ | | | 1.771 | 104.7 | 113.0 | −5.5 |
| t | t | $(c\text{-}t)^-$ | 1.758 | 103.9 | 113.4 | 3.1 |
| $g^+$ | | | 1.771 | 104.7 | 113.0 | 5.5 |
| $g^-$ | | | 1.771 | 104.7 | 113.0 | 5.5 |
| t | t | c-c | 1.759 | 103.8 | 113.3 | −3.1 |
| $g^+$ | | | 1.771 | 104.7 | 112.9 | 2.0 |
| $g^-$ | | | 1.771 | 104.7 | 112.9 | −2.0 |
| | | | bond b | | | |
| t | t-t | t | 5.789 | 113.0 | 113.0 | 0.0 |
| | $(t\text{-}c)^+$ | | 5.789 | 113.2 | 113.2 | 70.8 |
| | $(t\text{-}c)^-$ | | 5.789 | 113.2 | 113.2 | −70.8 |
| | $(c\text{-}t)^+$ | | 5.787 | 113.4 | 113.4 | 106.3 |
| | $(c\text{-}t)^-$ | | 5.787 | 113.4 | 113.4 | −106.3 |
| | c-c | | 5.788 | 113.3 | 113.3 | 180.0 |
| | | | bond d (g) | | | |
| t | t | t | 1.831 | 103.6 | 109.1 | 3.7 |
| | $g^+$ | | 1.830 | 104.4 | 113.5 | 96.9 |
| | $g^-$ | | 1.830 | 104.4 | 113.5 | −96.9 |
| | t | $g^+$ | 1.834 | 103.5 | 110.7 | 1.3 |
| | $g^+$ | | 1.833 | 104.2 | 114.8 | 96.0 |
| | $g^-$ | | 1.835 | 105.4 | 113.7 | −68.8 |
| | t | $g^-$ | 1.834 | 103.5 | 110.7 | −1.3 |
| | $g^+$ | | 1.835 | 105.4 | 113.7 | 68.8 |
| | $g^-$ | | 1.833 | 104.2 | 114.8 | −96.0 |
| | | | bond e (f) | | | |
| t | t | t | 1.534 | 109.1 | 110.1 | −0.8 |
| | $g^+$ | | 1.535 | 110.7 | 113.2 | 112.6 |
| | $g^-$ | | 1.535 | 110.7 | 113.2 | −112.6 |
| $g^+$ | t | | 1.533 | 113.5 | 110.2 | 1.5 |
| | $g^+$ | | 1.535 | 114.8 | 112.6 | 113.2 |
| | $g^-$ | | 1.536 | 113.7 | 113.2 | −112.5 |
| $g^-$ | t | | 1.533 | 113.5 | 110.2 | −1.5 |
| | $g^+$ | | 1.536 | 113.7 | 113.2 | 112.5 |
| | $g^-$ | | 1.535 | 114.8 | 112.6 | −113.2 |
| t | t | $g^+$ | 1.534 | 109.1 | 113.2 | 4.3 |
| | $g^+$ | | 1.535 | 110.4 | 116.2 | 114.0 |
| | $g^-$ | | 1.536 | 112.5 | 117.1 | −101.3 |
| $g^+$ | t | | 1.533 | 113.6 | 113.2 | 5.9 |
| | $g^+$ | | 1.534 | 114.6 | 115.9 | 117.8 |
| | $g^-$ | | 1.535 | 115.6 | 117.1 | −104.7 |
| $g^-$ | t | | 1.533 | 113.2 | 113.2 | 2.8 |
| | $g^+$ | | 1.534 | 113.0 | 115.1 | 107.4 |
| | $g^-$ | | 1.536 | 115.9 | 116.3 | −98.2 |
| t | t | $g^-$ | 1.534 | 109.1 | 113.2 | −4.3 |
| | $g^+$ | | 1.536 | 112.5 | 117.1 | 101.3 |
| | $g^-$ | | 1.535 | 110.4 | 116.2 | −114.0 |
| $g^+$ | t | | 1.533 | 113.2 | 113.2 | −2.8 |
| | $g^+$ | | 1.536 | 115.9 | 116.3 | 98.2 |
| | $g^-$ | | 1.534 | 113.0 | 115.1 | −107.4 |
| $g^-$ | t | | 1.533 | 113.6 | 113.2 | −5.9 |
| | $g^+$ | | 1.535 | 115.6 | 117.1 | 104.7 |
| | $g^-$ | | 1.534 | 114.6 | 115.9 | −117.8 |

[a] $j$ denotes the current bond. The blank line represents that the conformation is inexistent. [b]Length of bond $j$ in Å. [c]Angle formed between bonds $j-1$ and $j$ in deg. [d]Angle formed between bonds $j$ and $j+1$ in deg. [e]Dihedral angle of bond $j$ in deg.

**Table S7** Average geometrical parameters of PA2T, PA3T, PTA2T, and PTA3T

| | | | | dihedral angle (°) | | | |
|---|---|---|---|---|---|---|---|
| | bond | bond length (Å) | bond angle (°) | $\phi_{t}$ or $\phi_{t-t}$ | $\phi_{g^{\pm}}$ or $\phi_{(t-c)^{\pm}}$ | $\phi_{(c-t)^{\pm}}$ | $\phi_{c-c}$ |
| PA2T | a | 1.360 | 117.5 | 0.1 | | | |
| | b | 5.810 | 117.5 | 0.0 | ±53.6 | ±123.0 | 180.0 |
| | c | 1.360 | 122.5 | 0.1 | | | |
| | d | 1.458 | 112.9 | 0.0 | ±92.2 | | |
| | e | 1.529 | 112.9 | 0.2 | ±113.9 | | |
| | f | 1.458 | 122.5 | 0.0 | ±92.2 | | |
| PA3T | a | 1.359 | 118.7 | 0.0 | | | |
| | b | 5.823 | 118.7 | 0.0 | ±46.9 | ±129.2 | 180.0 |
| | c | 1.359 | 123.0 | 0.0 | | | |
| | d | 1.458 | 112.8 | −19.0 | ±72.1 | | |
| | e | 1.531 | 112.8 | −0.2 | ±116.2 | | |
| | f | 1.531 | 112.8 | −0.2 | ±116.2 | | |
| | g | 1.458 | 123.0 | −19.0 | ±72.1 | | |
| PTA2T | a | 1.340 | 115.3 | 0.1 | | | |
| | b | 5.793 | 115.3 | 0.0 | ±79.6 | ±98.0 | 180.0 |
| | c | 1.340 | 125.8 | 0.1 | | | |
| | d | 1.457 | 112.4 | −2.2 | ±88.4 | | |
| | e | 1.529 | 112.4 | 0.0 | ±113.3 | | |
| | f | 1.457 | 125.8 | −2.2 | ±88.4 | | |
| PTA3T | a | 1.338 | 115.1 | 0.3 | | | |
| | b | 5.808 | 115.1 | 0.0 | ±75.8 | ±102.5 | 180.0 |
| | c | 1.338 | 125.9 | 0.3 | | | |
| | d | 1.459 | 111.7 | 4.0 | ±88.4 | | |
| | e | 1.529 | 112.4 | −0.2 | ±111.3 | | |
| | f | 1.529 | 111.7 | −0.2 | ±111.3 | | |
| | g | 1.459 | 125.9 | 4.0 | ±88.4 | | |

**Table S8** Average geometrical parameters of $P2TS_2$, $P3TS_2$, $P2TS_4$, and $P3TS_4$

| | | | | dihedral angle (°) | | | |
|---|---|---|---|---|---|---|---|
| | bond | bond length (Å) | bond angle (°) | $\phi_t$ or $\phi_{t-t}$ | $\phi_{g^\pm}$ or $\phi_{(t-c)^\pm}$ | $\phi_{(c-t)^\pm}$ | $\phi_{c-c}$ |
| $P2TS_2$ | a | 1.802 | 117.9 | 0.0 | | | |
| | b | 5.787 | 117.9 | 0.0 | | | 180.0 |
| | c | 1.802 | 99.4 | 0.0 | | | |
| | d | 1.832 | 113.1 | −0.2 | ±97.3 | | |
| | e | 1.523 | 113.1 | 0.0 | ±115.0 | | |
| | f | 1.832 | 99.4 | −0.2 | ±97.3 | | |
| $P3TS_2$ | a | 1.807 | 118.2 | 0.0 | | | |
| | b | 5.793 | 118.2 | 0.0 | | | 180.0 |
| | c | 1.807 | 99.0 | 0.0 | | | |
| | d | 1.837 | 113.6 | 0.0 | ±95.2 | | |
| | e | 1.532 | 113.3 | 0.0 | ±110.8 | | |
| | f | 1.532 | 113.6 | 0.0 | ±110.8 | | |
| | g | 1.837 | 99.0 | 0.0 | ±95.2 | | |
| $P2TS_4$ | a | 1.762 | 113.0 | 0.1 | | | |
| | b | 5.787 | 113.0 | 0.0 | ±71.5 | ±106.3 | 180.0 |
| | c | 1.762 | 104.5 | 0.1 | | | |
| | d | 1.826 | 113.3 | 1.2 | ±85.1 | | |
| | e | 1.525 | 113.3 | 0.0 | ±112.8 | | |
| | f | 1.826 | 104.5 | 1.2 | ±85.1 | | |
| $P3TS_4$ | a | 1.768 | 113.0 | 0.0 | | | |
| | b | 5.788 | 113.0 | 0.0 | ±70.8 | ±106.3 | 180.0 |
| | c | 1.768 | 104.3 | 0.0 | | | |
| | d | 1.832 | 113.3 | 0.8 | ±91.3 | | |
| | e | 1.534 | 113.7 | 0.0 | ±110.4 | | |
| | f | 1.534 | 113.3 | 0.0 | ±110.4 | | |
| | g | 1.832 | 104.3 | 0.8 | ±91.3 | | |