Supplementary Content

Photoemission spectroscopy of rubrene thin films doped with heavy alkali metal: A first-principles investigation

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1 Relativistic effects of heavy alkali

The relativistic effects of heavy alkali on the isomeric complexes are calculated by mixed basis sets techniques, where the SPK\textsubscript{D}ZC basis set\textsuperscript{1–3} of GAMESS and the DZP-DKH basis set\textsuperscript{4,5} of EMSL are mixed. The EDOS of Cs\textsubscript{1}Rub and Rb\textsubscript{1}Rub isomers are shown in Figs. S1 and S2, respectively. In both figures, subplots (a) and (b) are the EDOS calculated without and with DKH corrections, respectively. It is found that for both figures, the EDOS in subplots (a) and (b) are almost indistinguishable, suggesting that the relativistic effects of heavy alkali are weak in alkali-rubrene complexes.

2 Electronic structures of minimum-energy Rb\textsubscript{1}Rub

The electronic structures of minimum-energy Rb\textsubscript{1}Rub isomers in D\textsubscript{2h} and C\textsubscript{2v}\textsubscript{h}-like conformations are shown in Figs. S3 and S4, respectively. The electronic structures of minimum-energy Rb\textsubscript{1}Rub are very similar to those of minimum-energy Cs\textsubscript{1}Rub shown in Figs. 4 and 5 of the main text.

References


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Fig. S1 The EDOS of Cs$_2$Rub isomers calculated without and with DKH corrections are shown in subplots (a) and (b), respectively. Isomer structures are shown in the insets next to their corresponding EDOS spectra. Curves [(c) to (f) and (k) to (n)] and [(g) to (j) and (o) to (r)] are the EDOS of $D_2$- and $C_{2h}$-like Cs$_2$Rub isomers, respectively, arranged in the order of increasing energy.
The EDOS of Rb$_2$Rub isomers calculated without and with DKH corrections are shown in subplots (a) and (b), respectively. The meanings of all other aspects of this plot are same as Fig. S1.
Fig. S3  The electronic structures of the $D_2$-like minimum-energy Rb$_1$Rub complex are plotted. The total EDOS is decomposed with methods same as Fig. 4 of the main text.
**Fig. S4** The electronic structures of the $C_{2h}$-like minimum-energy Rb$_1$Rub complex are plotted. The total EDOS is decomposed with methods same as Fig. 5 of the main text except that the first group of backbone carbons (BACKBONE C GROUP 1) contains the four backbone carbons (C7, C6a, C10a, and C10 in Fig. 1 of the main text) nearest to the rubidium element, while the remaining 14 carbons constitute the second group (BACKBONE C GROUP 2).