Supplementary Material (ESI) for Chemical Communications

Crystallographic observation of an olefin photodimerization reaction that takes place *via* thermal molecular tumbling within a self-assembled host

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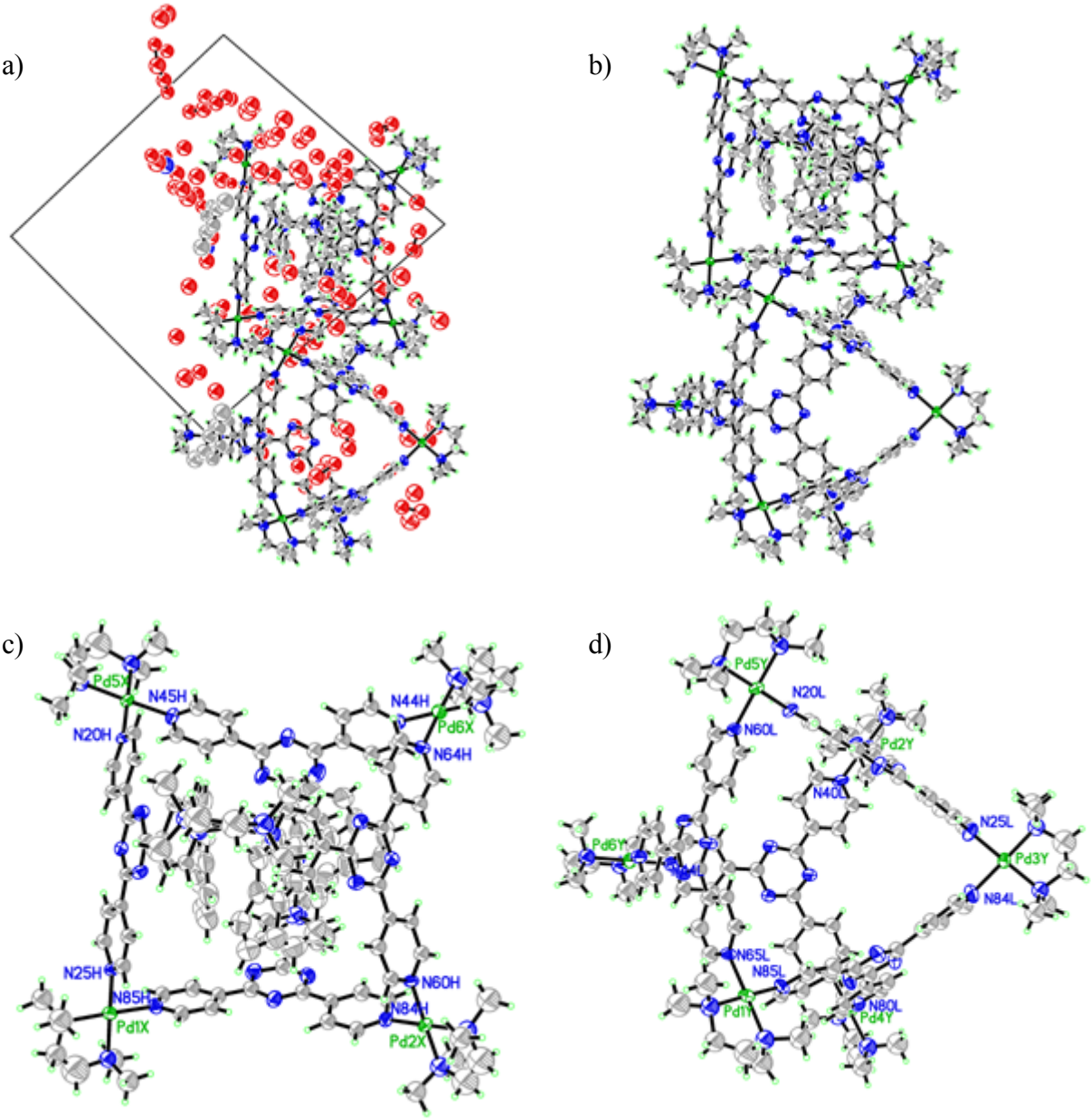

Fig. S1 ORTEP view (30% probability level) of $[\mathbf{1}_A\supset(\mathbf{2})_2]$ $[\mathbf{1}_B\supset\mathbf{2}]$ •**2** measured a Bruker APEX-II/CCD at 240 K: a) crystal structure of $[\mathbf{1}_A\supset(\mathbf{2})_2]$ $[\mathbf{1}_B\supset\mathbf{2}]$ •**2** with NO_3 ions and oxygen atoms around the cage: the number of electron density peaks corresponding to water molecules considerably decreased, compared with 90 K. b) crystal structure of $[\mathbf{1}_A\supset(\mathbf{2})_2]$ $[\mathbf{1}_B\supset\mathbf{2}]$, c) molecular structure of $\mathbf{1}_A$ and acenaphthylenes, d) molecular structure of $\mathbf{1}_B$ (guest molecules were not confirmed by X-ray analysis because of severe disorder). The thermal temperature factors of palladium atoms, nitrogen atoms of triazine ligands, and carbon atoms of acenaphthylenes were anisotropically refined, and those of other molecules isotropically. Several restraints were applied to the protection groups of N,N,N',N'-tetramethyl-entylenediamine in **1**, disordered NO_3 ions and water molecules.

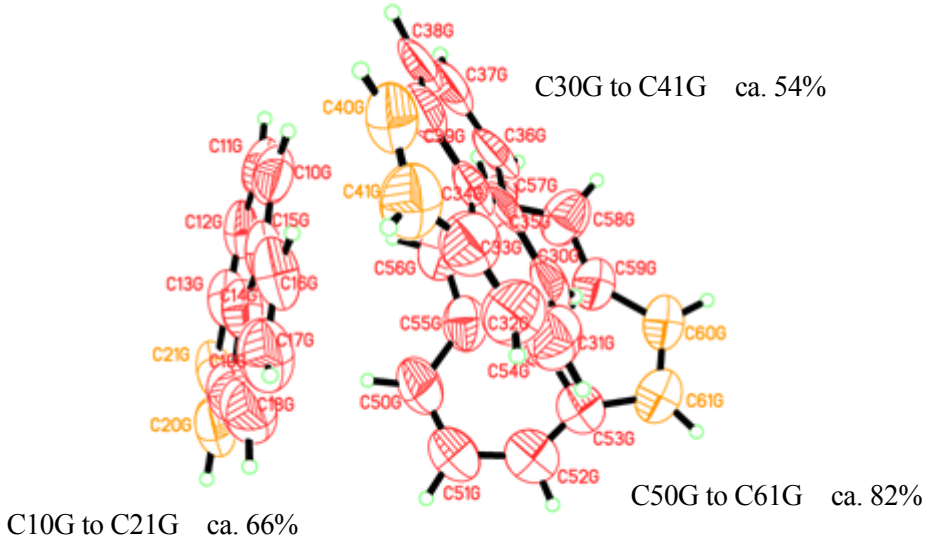

Fig. S2 ORTEP view (30% probability level) with the occupancy of disordered acenaphthylene molecules in $\mathbf{1}_A$ at 240 K:

Guest molecules migrated to the most stable geometries by thermal activation via rotational and flipping motions. Center-to-center distances between C=C bonds among three disordered acenaphthylene guests are 8.3 Å (C20G=C21G and C40G=C41G), 9.0 Å (C40G=C41G and C60G=C61G), and 8.4 Å (C60G=C61G and C20G=C21G). Intermolecular diene units are twisted with torsion angles of 19.3º (C20G=C21G and C40G=C41G), 17.9º (C40G=C41G and C60G=C61G), and 34.1º (C60G=C61G and C20G=C21G). The thermal temperature factors of acenaphthylene molecules were anisotropically refined. Several restraints were applied to disordered guests.

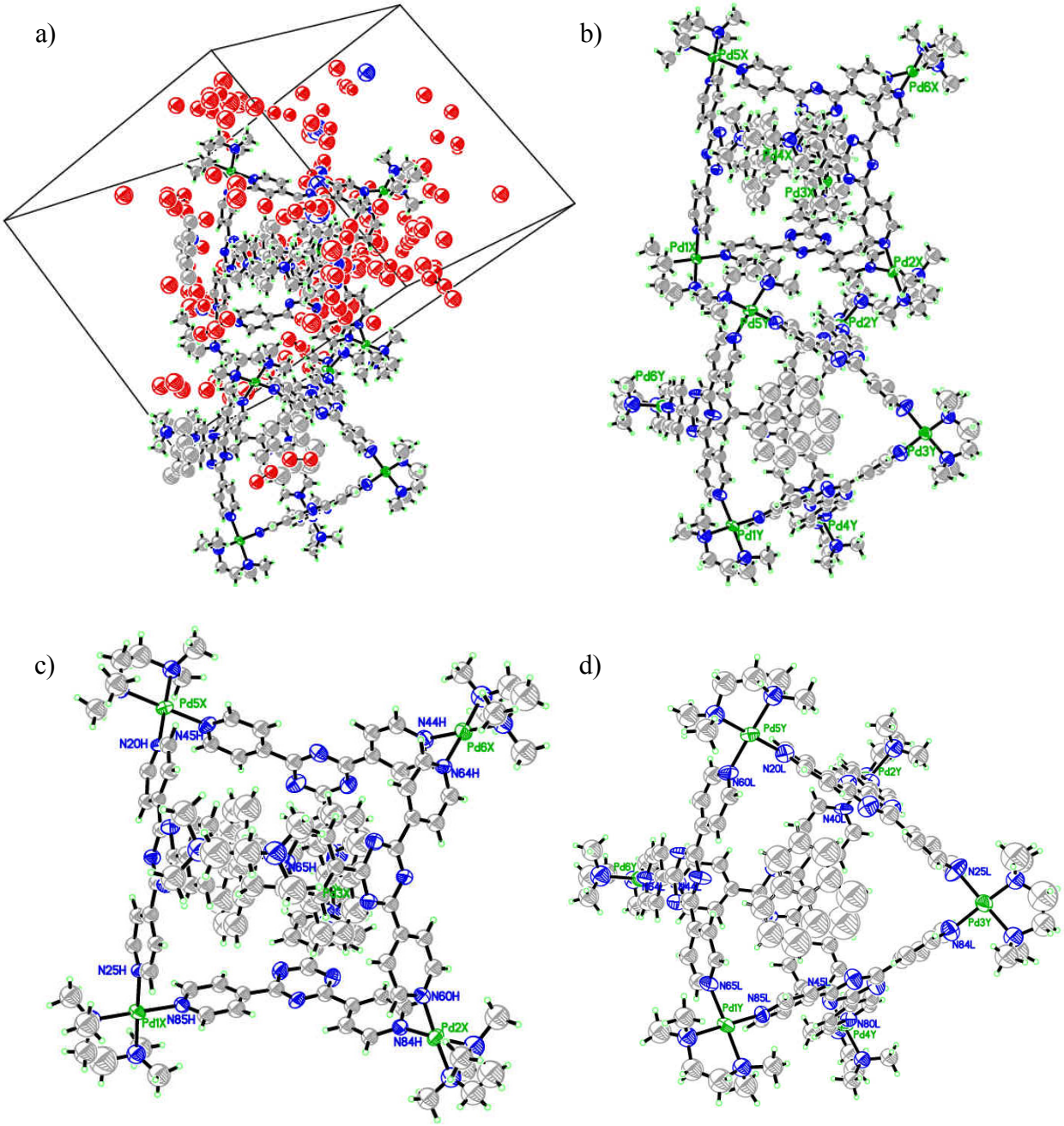

Fig. S3 ORTEP view (30% probability level) of [$\mathbf{1_A}\supset\mathbf{3}$] [$\mathbf{1_B}\supset\mathbf{2}$] •**2**: a) crystal structure of [$\mathbf{1_A}\supset\mathbf{3}$] [$\mathbf{1_B}\supset\mathbf{2}$] •**2** with NO_3 ions and oxygen atoms around the cage, b) crystal structure of [$\mathbf{1_A}\supset\mathbf{3}$] [$\mathbf{1_B}\supset\mathbf{2}$] •**2**, c) molecular structure of $\mathbf{1_A}$ and syn-dimer **3**, d) molecular structure of $\mathbf{1_B}$ and acenaphthylene (**2**). The thermal temperature factors of palladium atoms and nitrogen atoms of triazine ligands were anisotropically refined, and those of other molecules isotropically. Several restraints were applied to the protection groups of N,N,N',N'-tetramethyl-entylenediamine in **1**. Several restraints and constraints were applied to highly disordered NO_3 ions and water.

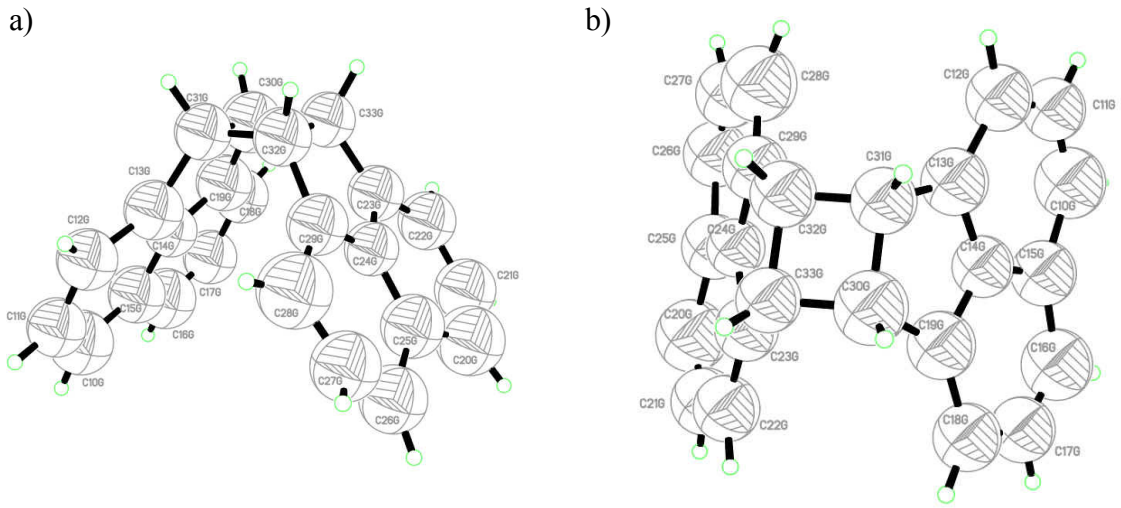

Fig. S4 ORTEP view (30% probability level) of syndimer **3** in $\mathbf{1}_{\mathbf{A}}$: a) side view, b) top view. The thermal temperature factors of **3** were isotropically refined. Several restraints were applied to **3** on a basis of chemical symmetry of the molecules.

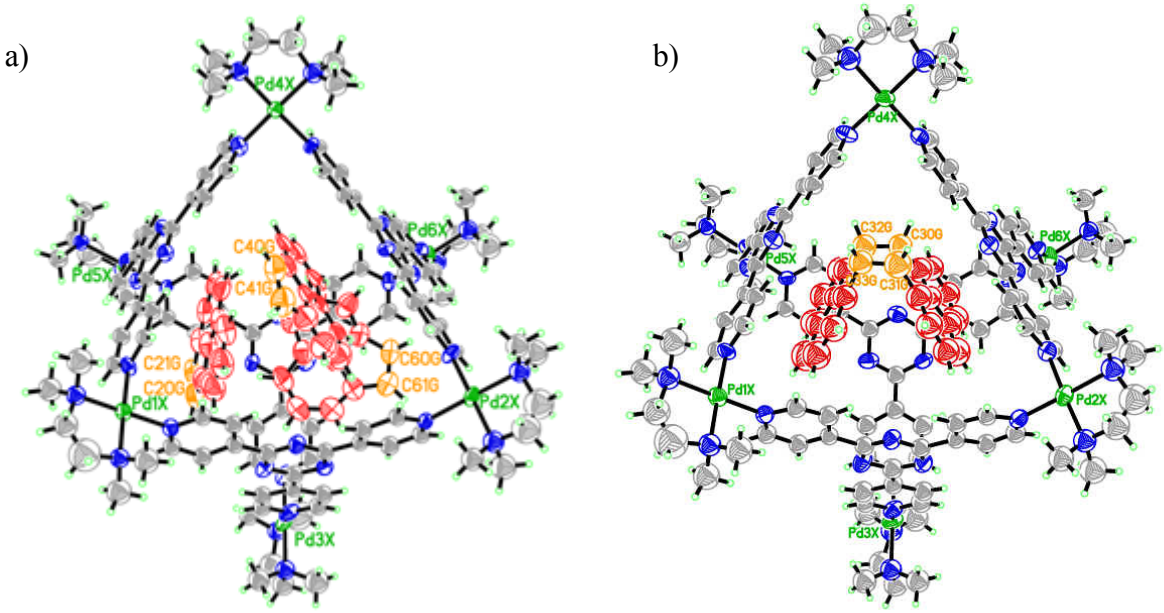

Fig. S5 The change of the molecular structure of $\mathbf{1}_{\mathbf{A}}$ and guest molecules by UV-irradiation: a) before irradiation, b) after irradiation (ORTEP view, 30% probability level).

X-ray Single Crystal Analysis of [$\mathbf{1}_A\supset(\mathbf{2})_2$] [$\mathbf{1}_B\supset\mathbf{2}$] •**2** at 90 K (before irradiation): The X-ray crystallographic measurement was performed on PF-AR NW2 beamline (λ(synchrotron) = 0.6890 Å) at High Energy Accelerator Research Organization (KEK), Japan. Diffraction data were collected at 90 K (before irradiation) and 240 K (after irradiation) at the same crystal throughout the experiment. The structures were solved by direct methods (SHELXS 97) and refined by full-matrix least-squares calculations on F^2 (SHELXL-97) using the SHELX-TL program package. Hydrogen atoms were fixed at calculated positions and refined using a riding model.

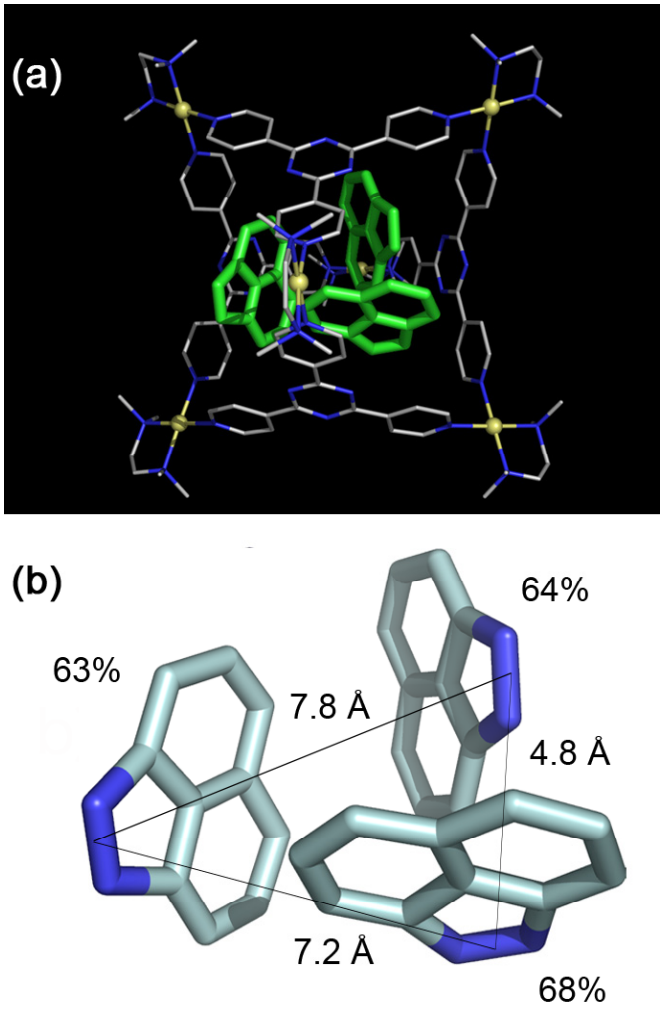

Fig. S6 (a) The crystal structure of $\mathbf{1}_A\supset(\mathbf{2})_2$ at 90 K. Counter ions, solvents of crystallization, coexisting $\mathbf{1}_B\supset\mathbf{2}$, and a free acenaphthylene molecule (per two cages) are omitted. (b) The geometrical relationship among the two guests disordered at three positions in $\mathbf{1}_A$. Percentages indicate the occupancies of the guests.

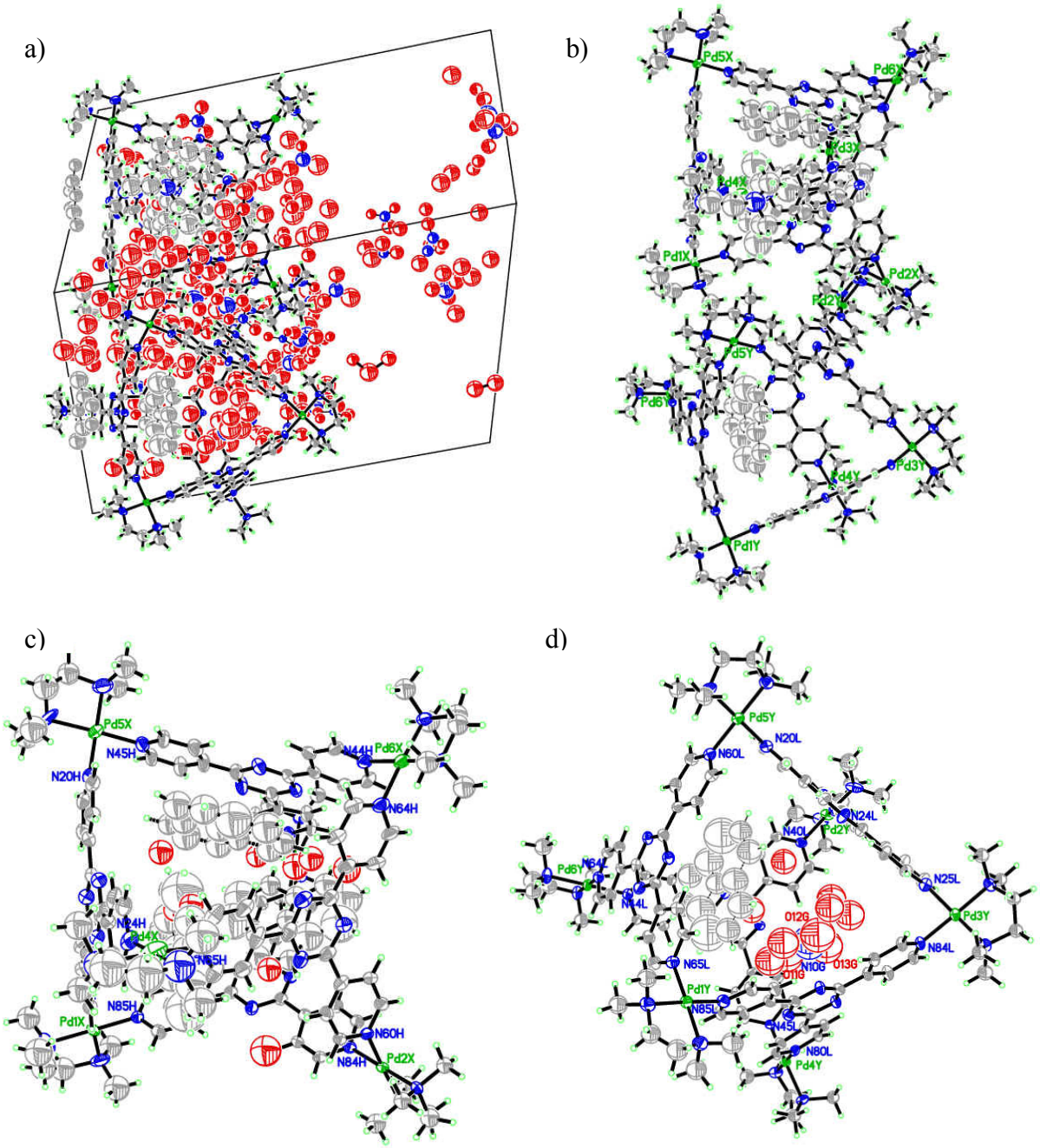

Fig. S7 ORTEP view (30% probability level) of $[\mathbf{1}_{\mathbf{A}}\supset(\mathbf{2})_2]$ $[\mathbf{1}_{\mathbf{B}}\supset\mathbf{2}]$ •**2** at 90 K: a) crystal structure of $[\mathbf{1}_{\mathbf{A}}\supset(\mathbf{2})_2]$ $[\mathbf{1}_{\mathbf{B}}\supset\mathbf{2}]$ •**2** with NO_3 ions and oxygen atoms around the cage, b) crystal structure of $[\mathbf{1}_{\mathbf{A}}\supset(\mathbf{2})_2]$ $[\mathbf{1}_{\mathbf{B}}\supset\mathbf{2}]$, c) molecular structure of $\mathbf{1}_{\mathbf{A}}$ and guest molecules (acenaphthylene and water), d) molecular structure of $\mathbf{1}_{\mathbf{B}}$ and guest molecules (acenaphthylene, NO_3 ions and water). The thermal temperature factors of palladium atoms and triazine ligands were anisotropically refined, and those of other molecules isotropically. Several restraints were applied to the protection groups of N,N,N',N'-tetramethyl-entylenediamine in **1**. Several restraints and constraints were applied to disordered NO_3 ions and water molecules.

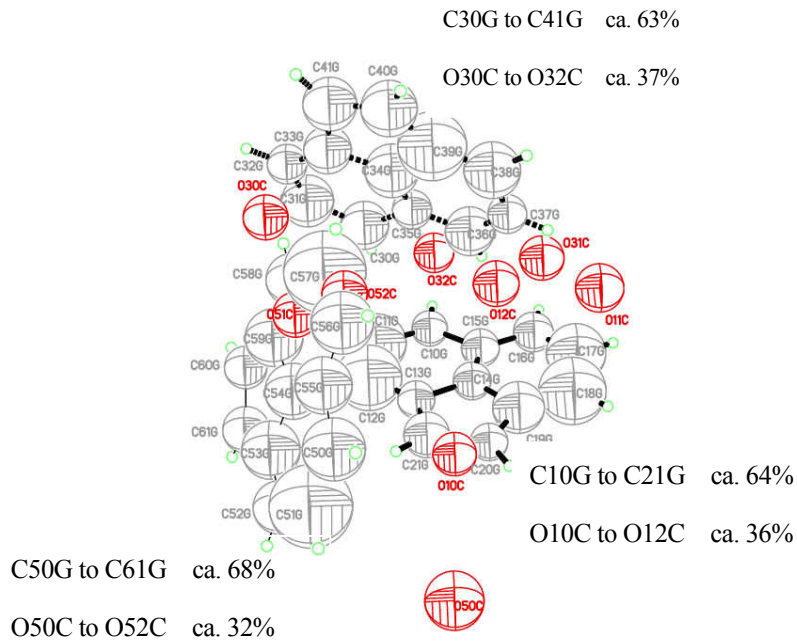

Fig. S8 ORTEP view (30% probability level) with the occupancy of disordered guest molecules (acenaphthylene and water) in $\mathbf{1}_{\mathbf{A}}$ before irradiation at 90 K:

Center-to-center distances between C=C bonds among three disordered acenaphthylene guests are 7.8 Å (C20G=C21G and C40G=C41G), 7.2 Å (C40G=C41G and C60G=C61G), and 4.8 Å (C60G=C61G and C20G=C21G). Intermolecular diene units are twisted with torsion angles of 17.7º (C20G=C21G and C40G=C41G), 34.8º (C40G=C41G and C60G=C61G), and 41.3º (C60G=C61G and C20G=C21G). The thermal temperature factors of acenaphthylene molecules were isotropically refined because of their disorder. Several restraints and constraints were applied to disordered molecules on a basis of chemical symmetry of the molecules.

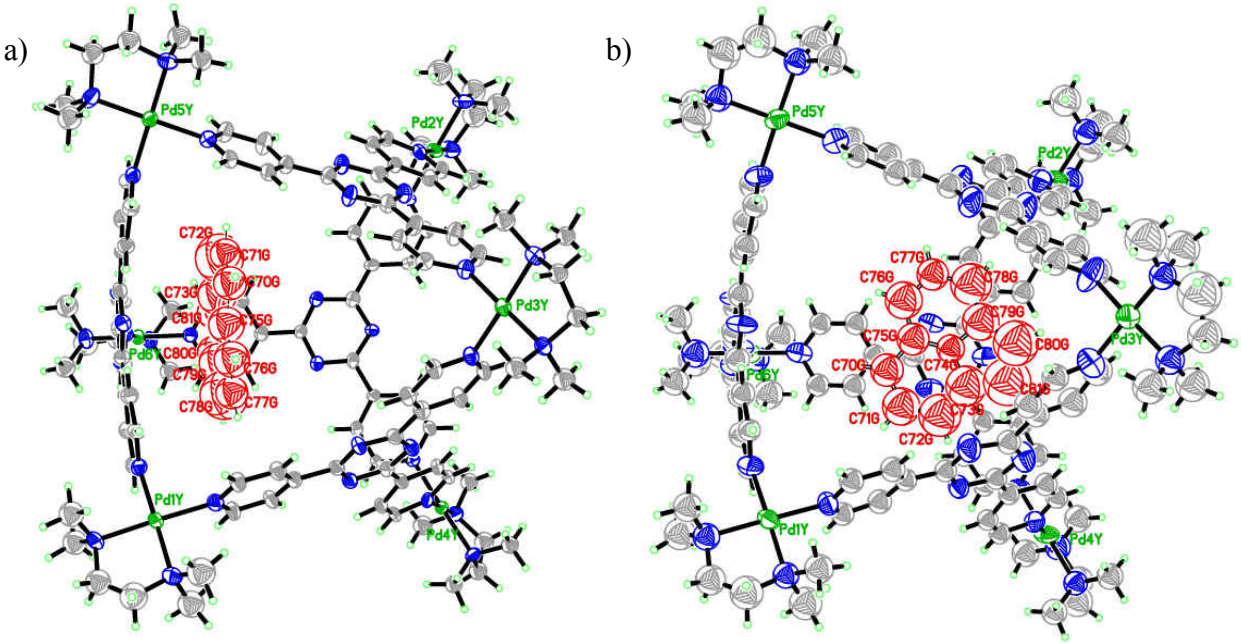

Fig. S9 The molecular structure of $\mathbf{1_B}$ and guest molecules (acenaphthylene): a) before irradiation at 90 K, b) after irradiation at 240 K (ORTEP view, 30% probability level). The occupancy of the disordered acenaphthylene in $\mathbf{1_B}$ converged to 74%.