Supporting Information

Photo-Oxidation of Trimethyl Phosphite in Nitrogen, Oxygen and Para-Hydrogen Matrixes at Low Temperatures

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Table S1. The dihedral angles of TMP and TMPhite.

Conformer	Phosphoryl group as reference	Adjacent P-O bond as reference
TMP		
C_3(GGG)	∠C6O3P1O2=44.8° ∠C7O4P1O2=44.8° ∠C8O5P1O2=44.7°	∠C6O3P1O4=-82.3° ∠C7O4P1O5=-82.3° ∠C8O5P1O3=-82.4°
C_1(TGG)	∠C6O3P1O2= 53.1° ∠C7O4P1O2=33.5° ∠C8O5P1O2=177.3	∠C6O3P1O4=-72.6° ∠C7O4P1O5=-92.9° ∠C8O5P1O3=49.4
Conformer	**P-X bond as reference (X=Dummy atom)**	**Adjacent P-O bond as reference**
TMPhite		
C_1(TGG)	∠C5O2P1X17=47.9°; ∠C6O3P1X17=54.0°; ∠C7O4P1X17=180°	∠C5O2P1O3=-71.3° ∠C6O3P1O4=-91.4° ∠C7O4P1O2=44.7°
C_3(GGG)	∠C5O2P1X17=36.3°; ∠C6O3P1X17=42.3°; ∠C7O4P1X17=55.9°	∠C5O2P1O3=-81.8° ∠C6O3P1O4=-81.6° ∠C7O4P1O2= -81.8

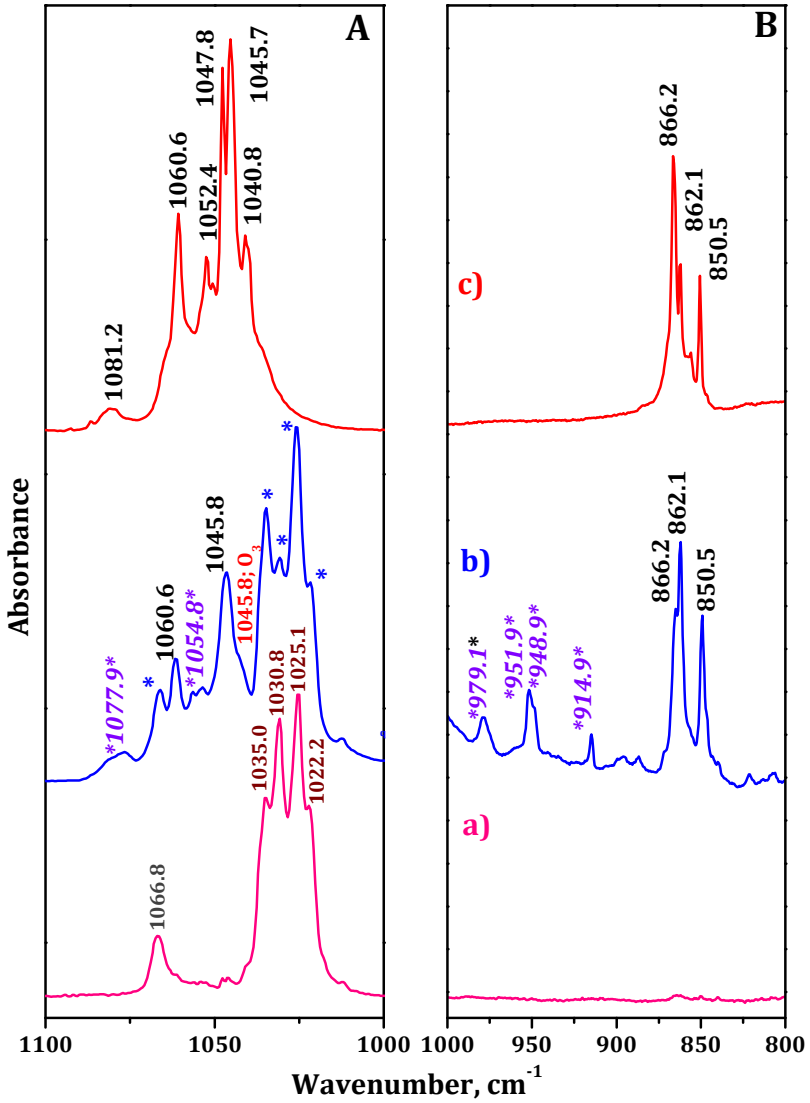

Figure S1. Infrared spectra of matrix isolated TMPhite with oxygen doped in N_2 matrix (grid 'A') O-C stretching and (grid 'B') P-O stretching regions. a) TMPhite/N_2 with 5 % O_2 before photolysis at 12 K, b) Same as in 'a' but photolysed for 30 minutes, c) TMP/N_2 with 5 % O_2 at 12 K. The TMPhite/TMP to N_2 ratio is 1:1000. The asterisk represents unreacted TMPhite precursor.

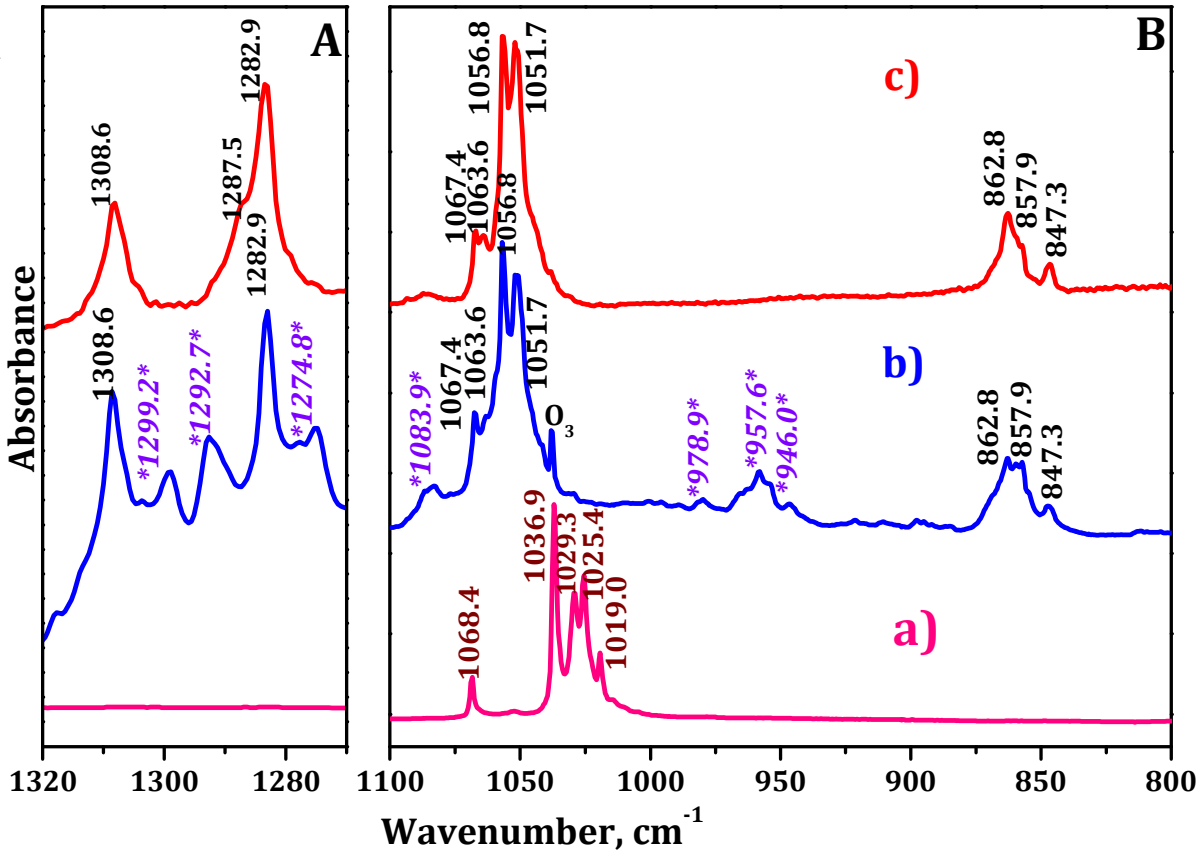

Figure S2. Infrared spectra of matrix isolated TMPhite in the oxygen matrix (grid A) P=O stretching region and (grid 'B') P-O and O-C stretching regions. a) TMPhite/O_2 before photolysis at 12 K, b) Same as in 'a' but photolysed for 30 minutes, c) TMP/O_2 at 12 K. The TMPhite/TMP to O_2 concentration is 1:1000.

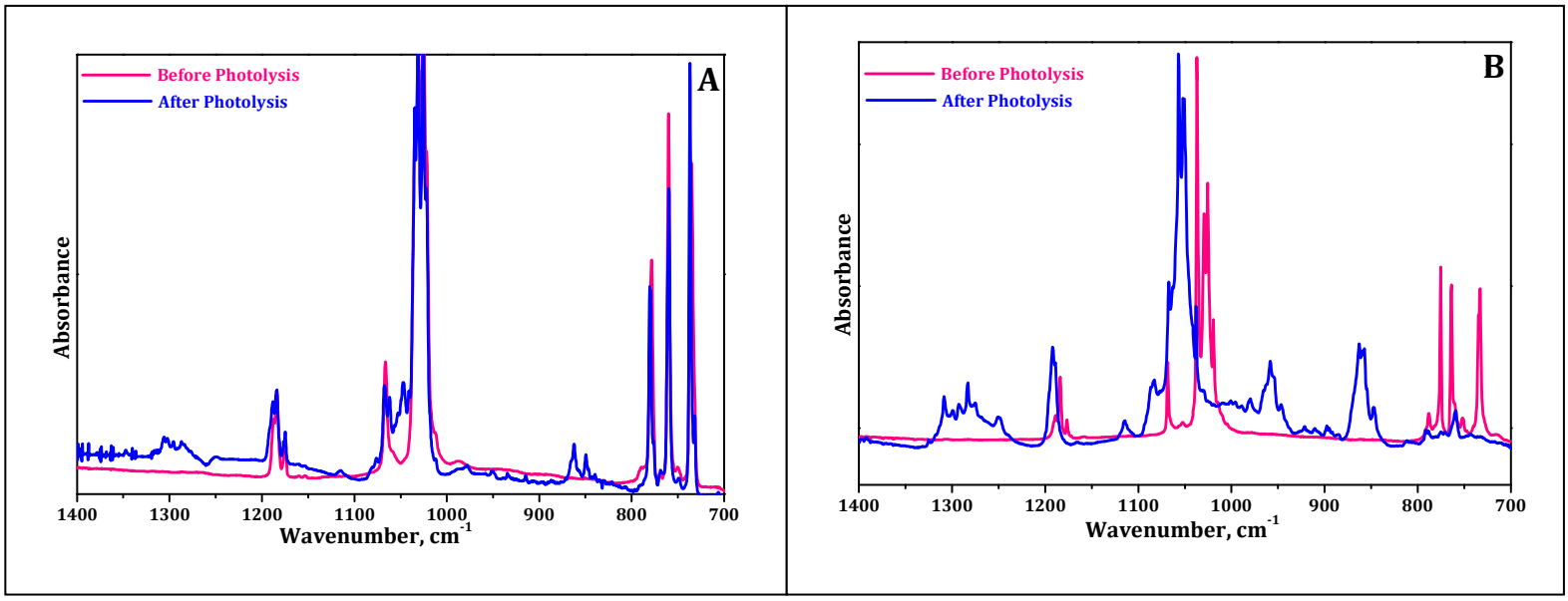

Figure S3. Infrared spectra of O_2 doped TMPhite before and after photolysis in the P=O, O-C and P-O stretching regions in N_2 matrix (grid 'A') and in O_2 matrix (grid 'B').

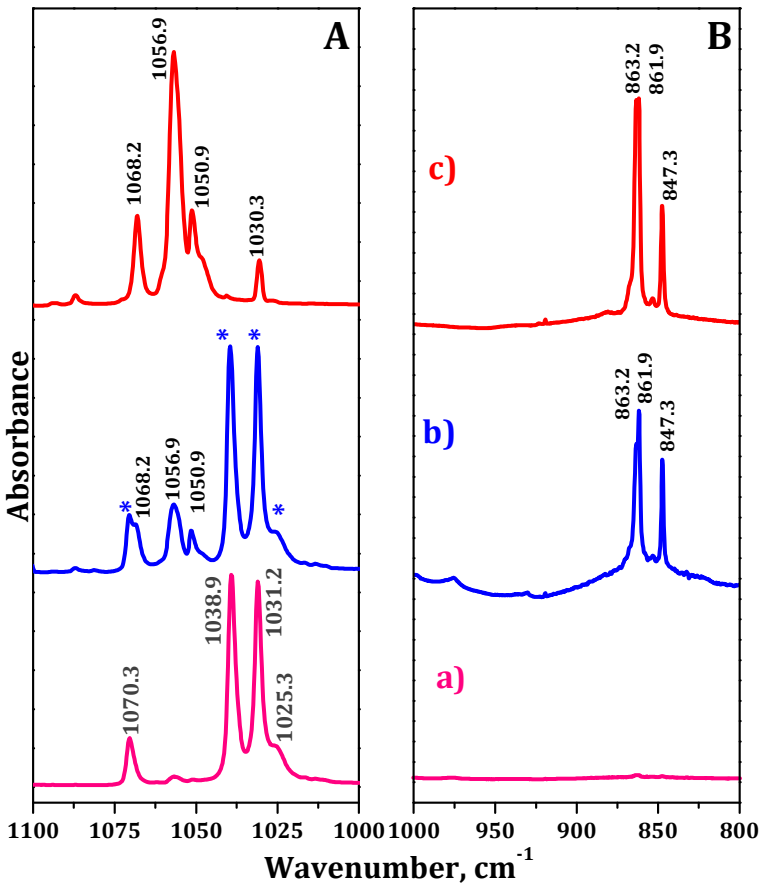

Figure S4. Infrared spectra of oxygen doped TMPhite in p-H_2 matrix (grid 'A') O-C stretching and (grid 'B') P-O stretching regions. a) TMPhite/p-H_2 with 5 % O_2 before photolysis at 2.5 K, b) Same as in 'a' but photolysed for 30 minutes, c) TMP/p-H_2 with 5 % O_2 at 2.5 K. The TMPhite /TMP to p-H_2 ratio is 1:1000. The asterisk represents unreacted TMPhite precursor.

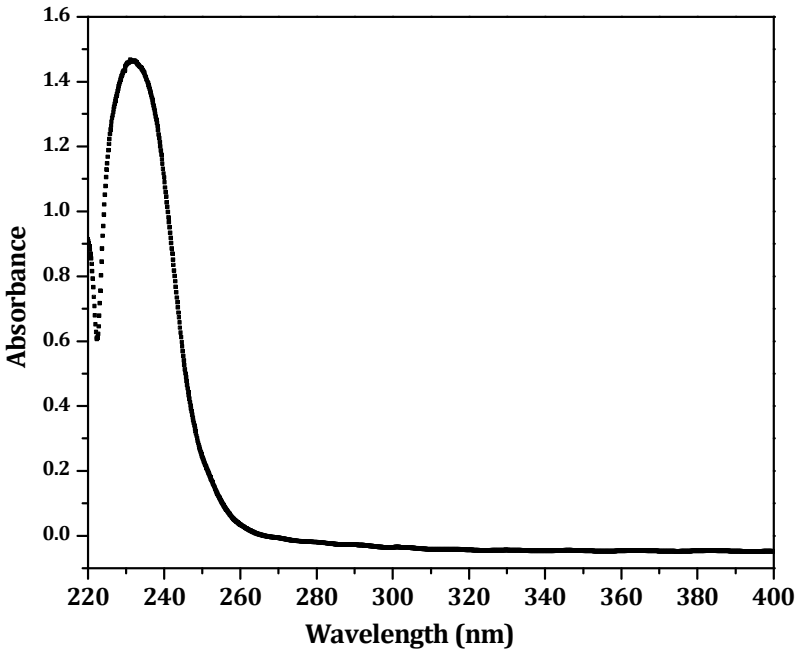

Figure S5. UV-Visible absorption spectrum of pure TMPhite.