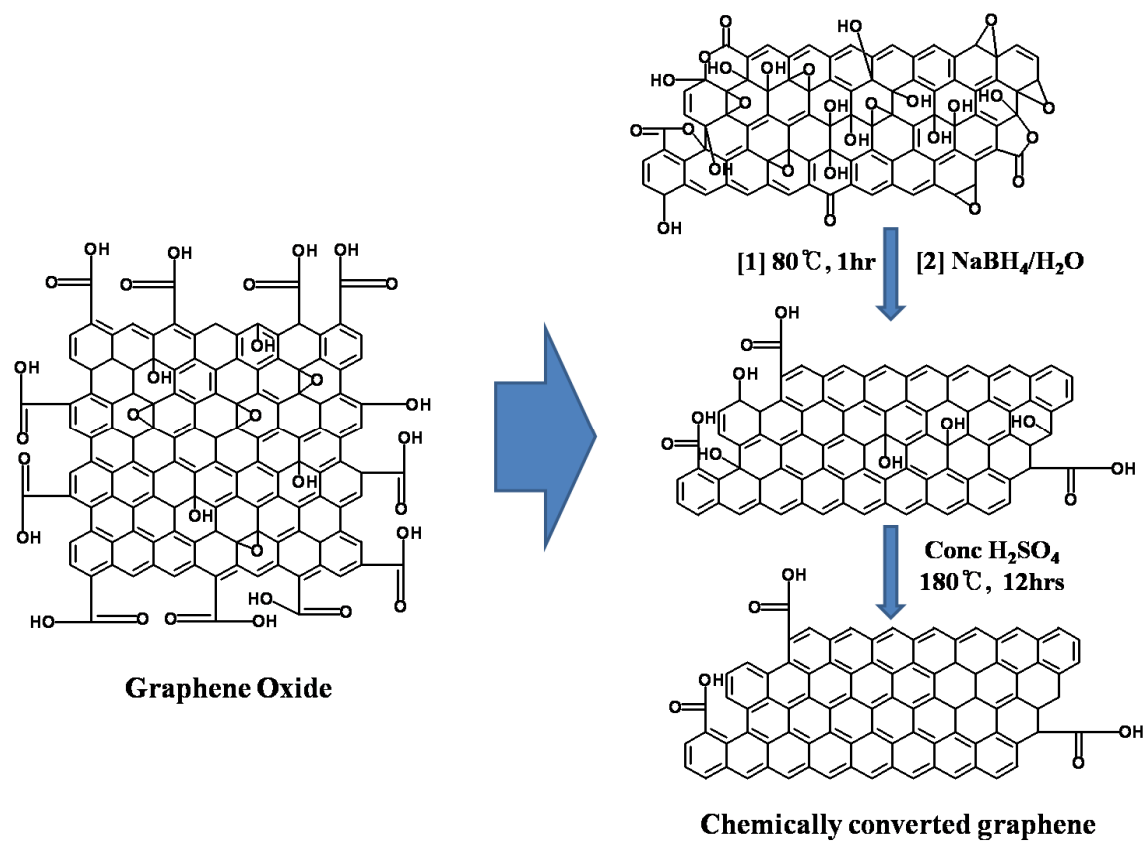


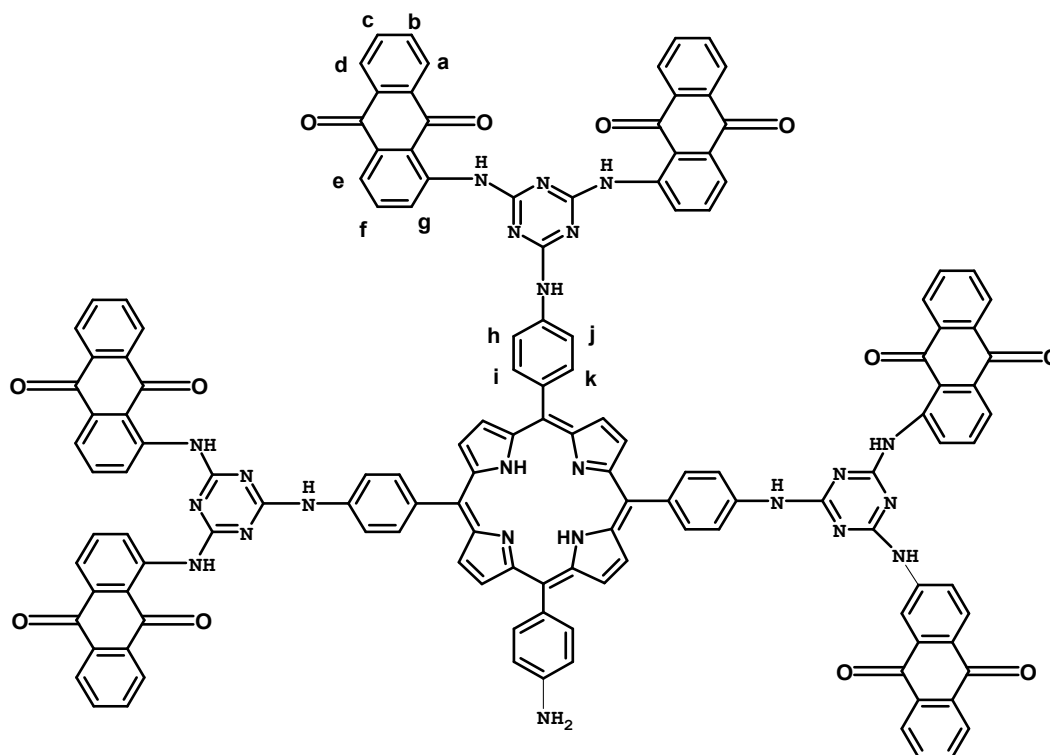
Supporting Information

A Photocatalyst-Enzyme Coupled Artificial Photosynthesis System for Solar Energy in Production of Formic Acid from CO₂

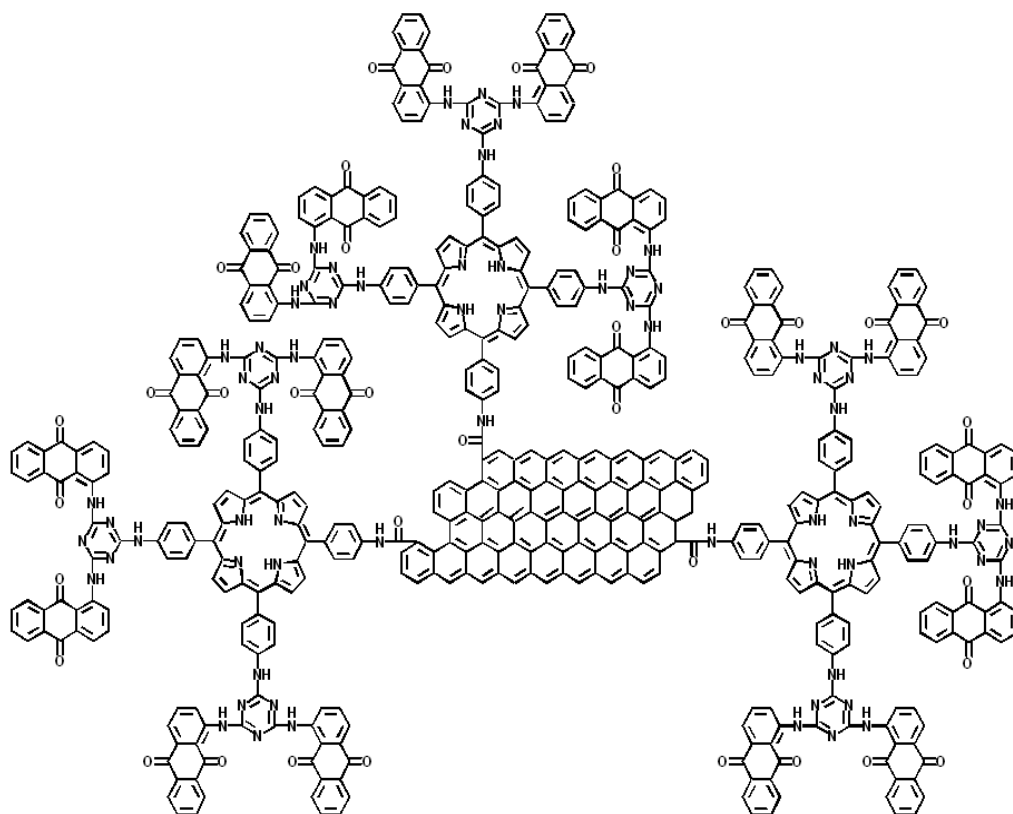
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Jinheung Kim,[‡] Dong Won Hwang,[†] and Soumya K. Biswas[†]



Scheme S1. Preparation of chemically converted graphene from graphene oxide



Scheme S2. Preparation of 5, 10, 15-[(4-{(3, 5-Tris-(Dichloro triazine)} aminophenyl)-20-aminophenyl porphyrin] Synthesis of 5, 10, 15-[(4-{(3, 5-Tris-(Diamino-anthraquinone)triazine} aminophenyl)-20-aminophenyl porphyrin]^{3,4}



Scheme S3. The graphene-based photocatalyst (CCGCMAQSP)

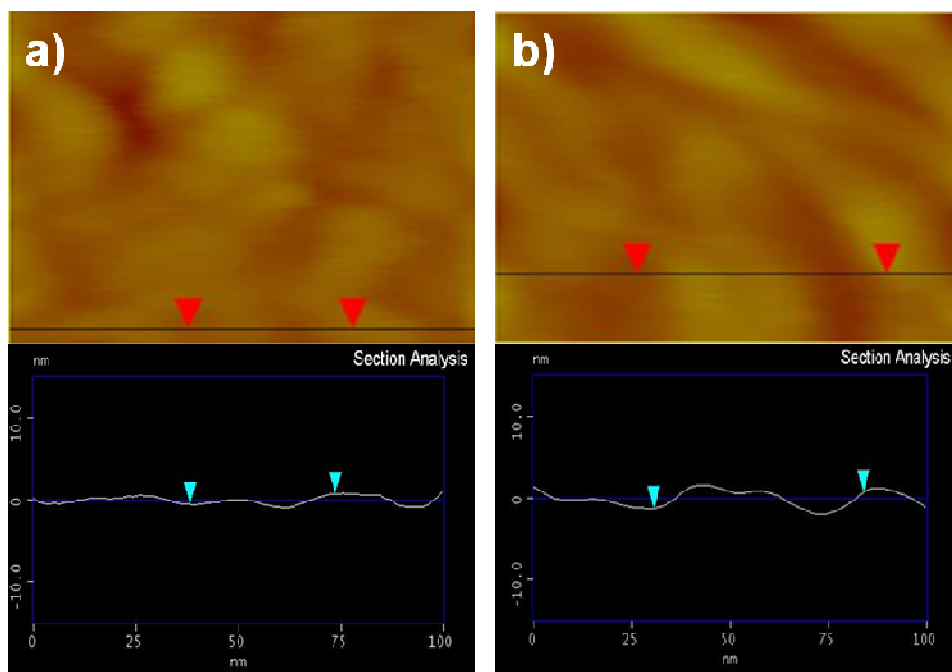


Figure S1. AFM images of a) CCG, b) CCGCMAQSP photocatalyst.

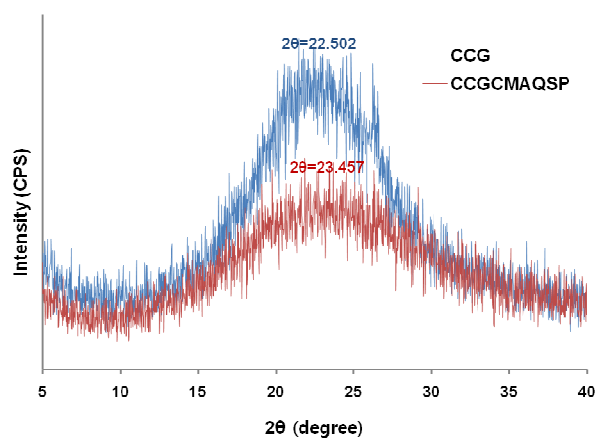


Figure S2. XRD data of chemically converted graphene (CCG) and chemically converted graphene coupled multi-anthraquinone substituted porphyrin (CCGCMAQSP). Fixed Time mode, step size 0.02 degree, dwell time 1 second. Wavelength to compute d -spacing 1.54059 Å, Cu/K-alpha 1.

For confirmation of the coupling of MAQSP with CCG, Raman (Model: Bruker/SENTERRA) studies were also carried out. The shape of the mode ($\sim 2680\text{ cm}^{-1}$)¹ and the relative intensities of the doubly degenerate mode ($\sim 1580\text{ cm}^{-1}$) were used to assess the number of layers present in the graphene samples.^{2,3} In uncorroded single-layer graphene, the disorder band of 1350 cm^{-1} was hardly noticeable but the 1350 cm^{-1} mode consequently developed after the oxidation began. There is a practical correlation between the intensity (I) ratio of the 1350 cm^{-1} mode to that of the 1625 cm^{-1} mode (I_{1350}/I_{1625}) as reported elsewhere.⁴ From the Raman spectra, it is obvious that the insignificant (I_{1350}/I_{1625}) ratio reveals the singularity of the CCG layer. Moreover, coupling of CCG with MAQSP leads to a shift in the band. The incorporation of MAQSP into the CCG material leads to a prominent Raman shift in the 2000 to 500 cm^{-1} region. We observed considerable shifts at the 1350 cm^{-1} and 1625 cm^{-1} bands of the spectra of CCGCMAQSP at 500 cm^{-1} and 1125 cm^{-1} , respectively.

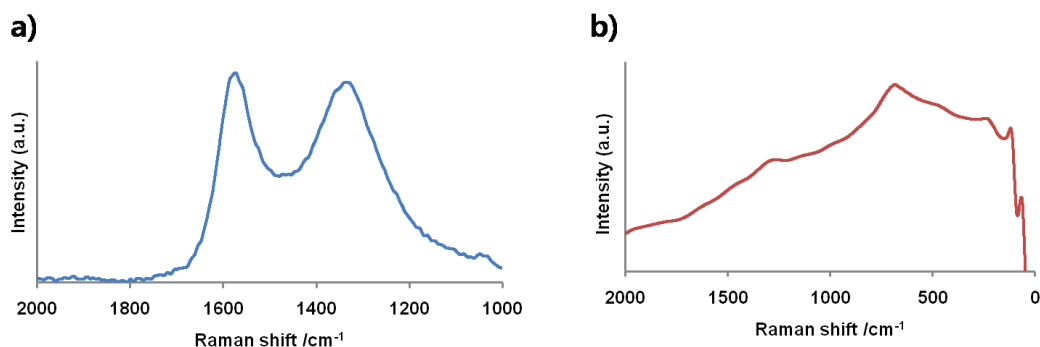


Figure S3. Raman spectra of a) chemically converted graphene (CCG), b) chemically converted graphene coupled multi-anthraquinone substituted porphyrin (CCGCMAQSP) (532 nm Laser beam, room temperature, solid samples on glass).

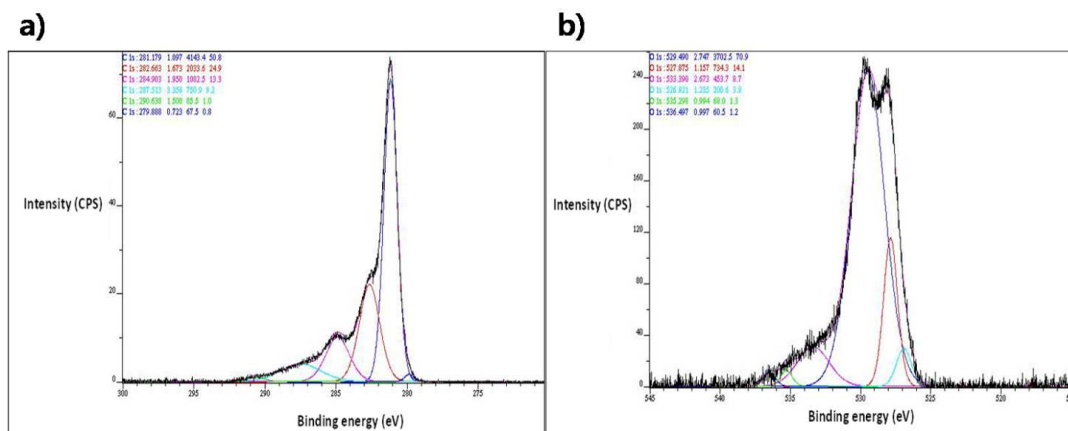


Figure S4. a) C 1s, b) O 1s XPS spectra of chemically converted graphene (CCG).

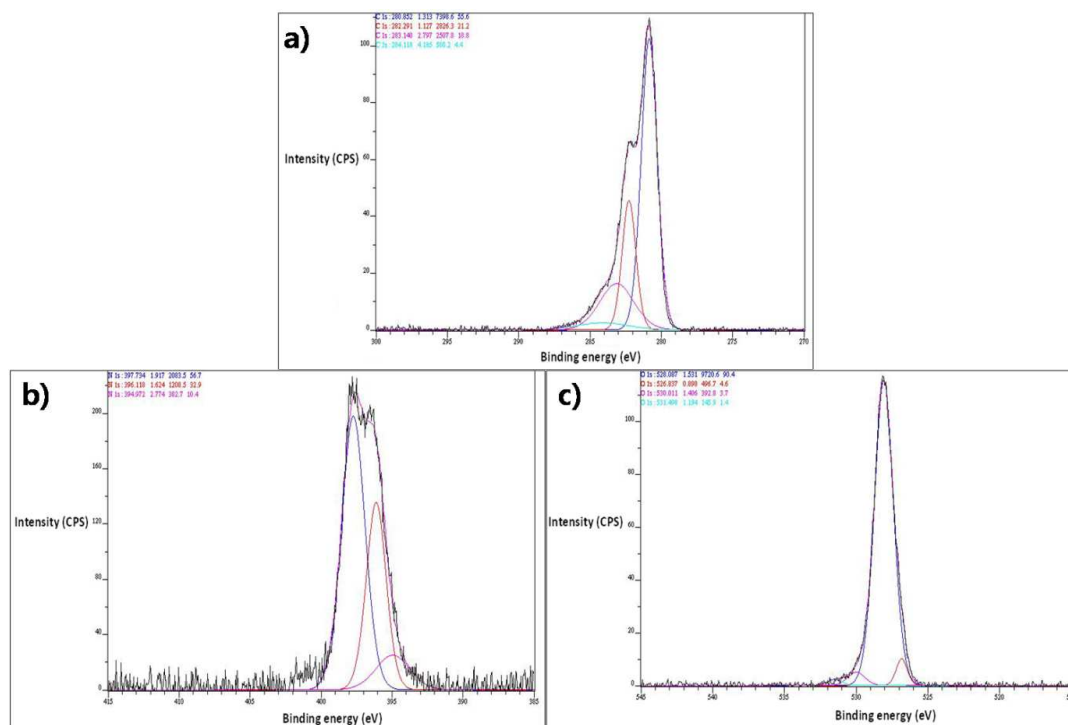


Figure S5. a) C 1s, b) N 1s, c) O 1s XPS spectra of chemically converted graphene coupled multi-anthraquinone substituted porphyrin (CCGCMAQSP).

The restoration of CCG to CCGCMAQSP in the existence of MAQSP was confirmed by XPS (Model: KARTOS AXIS NOVA). The XPS of CCG revealed significant peaks, C-C, C-O, C=O and O-C=O species, respectively. Additionally, compared to the spectrum of CCGCMAQSP, the intensity of the Oxygen 'O' 1s peak relative to the carbon 'C' 1s peak was reduced with the finding of the nitrogen 'N' 1s peak in the XPS survey. Meanwhile, a recent peak corresponding to the C-N species resulted from the bond formation⁵ with MAQSP appeared at 394.9 eV. Consequently, the C-N species analyzed from the coupling between the CCG and MAQSP was identified as enhanced sp² networks.⁶

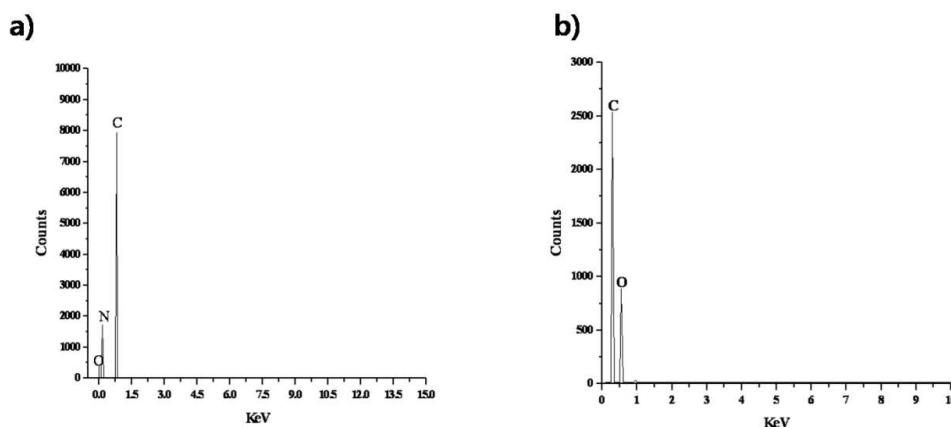


Figure S6. Energy-dispersive X-ray spectroscopy of a) chemically converted graphene (CCG), b) CCGCMAQSP.

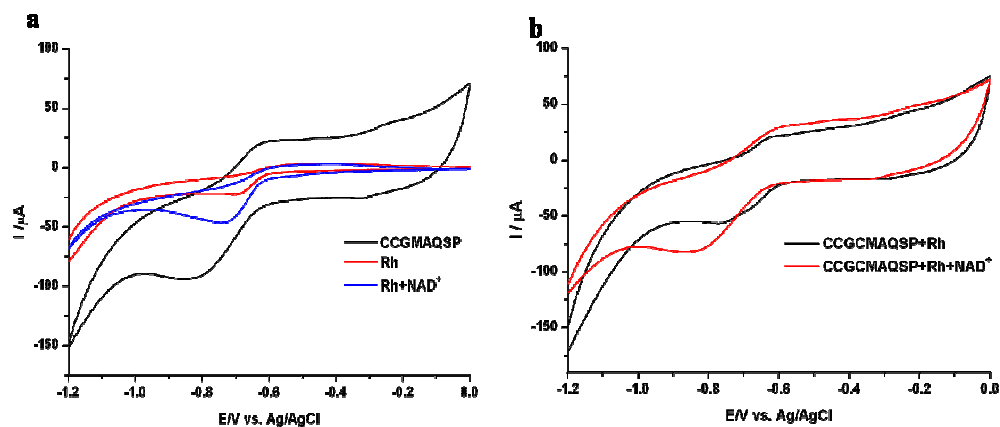


Figure S7. Cyclic voltammograms of (a) Rhodium complex (Rh) (0.2 mM), CCGCMAQSP (10 μM), and Rh with NAD⁺ (0.4 mM) solutions and (b) Mixture of two components in the presence and absence of NAD⁺ (0.4 mM). The potential was scanned at 100 mVs^{-1} .

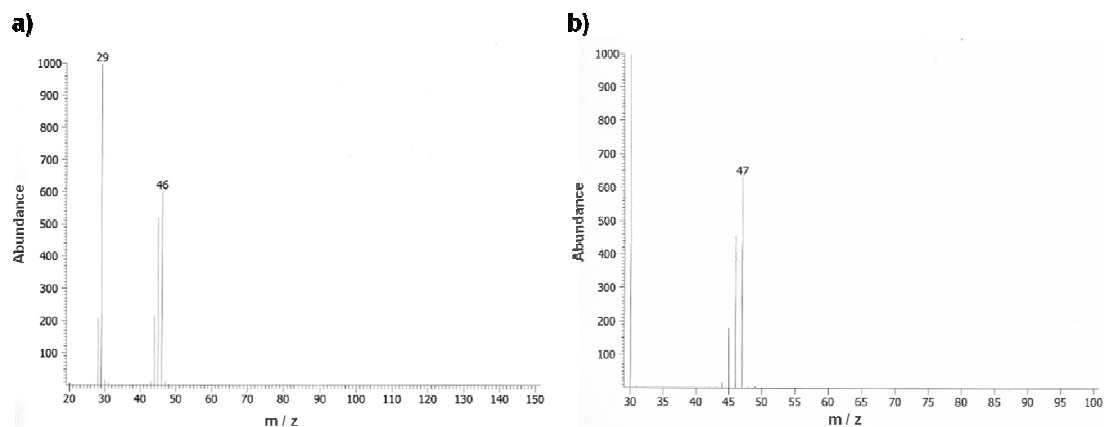


Figure S8. GC mass spectrometry data of a) formic acid from CO₂, b) formic acid from ¹³CO₂.

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