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<AT>Fabrication of covalently linked graphene-mediated [FeFe]-hydrogenases biomimetic photocatalytic hydrogen evolution system in aqueous solution

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<ABS-Head><ABS-HEAD>Graphical abstract
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<ABS-HEAD>Highlights► Graphene-mediated biomimetic photocatalytic system is fabricated in water. ► Organic photosensitizer and organometallic catalyst are covalently linked to GO. ► Effects of electron-transfer-pathway on H_2 production efficiency are analyzed. ► Two novel bionic H-cluster models are synthesized and characterized successfully. ► Positive result is earned by introducing cystine into photocatalytic system.

<ABS-HEAD>ABSTRACT
<ABS-P>Two novel complexes $[Fe_2(\mu\text{-}SC_3H_6S)(CO)_5][Fc(PPh_2)CHO]$ (**3**) and 5-{$[Fe_2(\mu\text{-}SC_3H_6S)(CO)_5](PPh_2Fc)$}-10, 15, 20-triphenylporphyrin (**4**), which contain ferrocene-based ligand to simulate the role of the active site of [FeFe]-hydrogenases (H-Cluster), are synthesized and characterized successfully. A graphene-mediated [FeFe]-hydrogenases biomimetic nanohybrid (TPP-NHCO-GO-[3Fe2S]) **6** is fabricated by linking organic photosensitizer tetraphenylporphyrin (TPP) and complex **3** to graphene oxide (GO) via the covalent bond. The new nanohybrid **6** is characterized by elemental analysis, FTIR, transmission electron microscopy (TEM) and inductively coupled plasma atomic emission spectrometry (ICP-AES). By comparing the ultraviolet-visible (UV-vis) absorption, fluorescence emission and time-resolved fluorescence, it could be found the efficiency of electron transfer has been obviously improved with the presence of GO, and the efficiency of electron transfer in intramolecular system is higher than that in intermolecular system. These results are also supported by the photo-induced H_2 production experiments with corresponding catalytic systems in water. Besides, the cystine is used as the sacrificial electron donor for light catalytic reaction in aqueous solution, which improves the efficiency of photocatalytic H_2 production compared with the common electron donors, such as ascorbic acid (H_2A), triethanolamine (TEOA), glucose or $Na_2S_2O_3$.