Communications

Microporous organic nanorods with electronic push–pull skeletons for visible light-induced hydrogen evolution from water†

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This work shows that microporous organic network (MON) chemistry can be successfully applied for the development of a visible light-induced hydrogen production system. A visible light harvesting MON (VH-MON) was prepared by the Knoevenagel condensation of tri-(4-formylphenyl)amine with [1,1’-biphenyl]-4,4’-diactonitile. Scanning electron microscopy (SEM) showed a 1D rod morphology of the VH-MON. Analysis of a N2 sorption isotherm showed a 474 m2 g−1 surface area and microporosity. Solid phase 13C nuclear magnetic resonance (NMR) and infrared (IR) absorption spectroscopy, and elemental analysis support the expected network structure. The VH-MON showed visible light absorption in 400–530 nm and vivid emission at 542 nm. The HOMO and LUMO energy levels of the VH-MON were simulated at −5.1 and −2.4 eV, respectively, by density functional theory (DFT) calculation. The VH-MON/TiO2–Pt composite exhibited promising activity and enhanced stability as a photocatalytic system for visible light-induced hydrogen production from water.

Recently, various microporous organic networks (MONs) have been prepared using organic building blocks.7 The robustness of covalent networks enables them to be applied for diverse purposes.2 For example, the MONs have shown good performance as gas adsorbents3 and heterogeneous catalysts.4 However, the use of MONs as visible light harvesting materials has been relatively less explored.5–7 The photoactive MONs can be simply obtained through the networking of light responsive building blocks.2 In another synthetic strategy, the crosslinking reactions can be utilized for the generation of target photoactive moieties in MONs.6 It has been well reported that electronic push–pull organic systems perform efficiently harvesting visible light in organic solar cells and photocatalysts.8 In this regard, the electron rich connectors and electron deficient building blocks can be connected during conjugated crosslinking for visible light responsive MONs. Although the photoactive MONs have been reported by our research group and others,5–7,9 delicate utilization of crosslinking steps for the formation of target photoactive moieties in MONs is relatively rare.6

Light-induced hydrogen evolution from water has attracted the continuous attention of scientists.7 Since the development of UV-based water photolysis systems using TiO2 and Pt catalysts,9 the dye-incorporated photocatalysts for the use of visible light have been extensively studied.10,11 In an earlier stage, ruthenium complexes have been studied as visible light harvesting dyes for hydrogen production from water.12 Recently, various organic dyes have been developed for more efficient visible light harvesting.13 Although single-molecular organic dyes have shown promising photocatalytic activities, their instability was a significant drawback. It can be speculated that the crosslinking of organic systems can enhance the stability of photocatalysts by kinetic suppression of decomposition pathways.14 Our research group has studied visible light-driven photocatalysts5,14 and functional MONs.15 In this work, we report the preparation of an MON containing electron rich triarylamino moieties and conjugated π-systems with cyano groups and its dye performance in visible light-induced hydrogen production from water.

Fig. 1 shows the synthetic scheme for the visible light harvesting MON (VH-MON). The crosslinking was based on Knoevenagel condensation between triformylarene and bicyanomethylenarene species.16 Triarylamino moieties have been used for light harvesting dyes due to their redox stability.17 Thus, tri(4-formylphenyl)-amine was prepared as a building block by a synthetic method in the literature.18 The [1,1’-biphenyl]-4,4’-diactonitile was prepared19 and used as another building block. In the Knoevenagel condensation of two building blocks, various bases and reaction conditions

† Electronic supplementary information (ESI) available: Additional SEM images of the VH-MON and organic materials prepared using different volumes of the solvent (THF), the TGA curve of the VH-MON, DFT calculation for model compounds of the VH-MON, SEM images of the VH-MON/TiO2–Pt composite before and after the five photocatalytic reactions, the results of hydrogen production using a mixture of a monomeric dye and TiO2–Pt, and the external quantum yield measurement. See DOI: 10.1039/c4ta00989d
such as solvents were screened for the optimized homogeneity of the resultant MON. When NaOH was used as a base in THF, the most interesting organic solids were obtained (see Fig. S1 and the ESI † for details of the procedure). The building blocks, tri(4-tert-butylphenyl)amine and [1,10-biphenyl]-4,4′-diacetonitrile, are pale yellow and white, respectively. In comparison, the resultant organic solids have a reddish color (Fig. 2a), indicating that the crosslinking was induced by Knoevenagel condensation. A similar trend of color change from yellow to reddish color through Knoevenagel condensation was observed in a non-polymeric model reaction using (4-formylphenyl)diphenylamine and 2-phenylacetonitrile.

The VH-MON was investigated by SEM, N₂ sorption isotherm analysis by the Brunauer-Emmett-Teller (BET) theory, and powder X-ray diffraction (PXRD) studies. As shown in Fig. 2a and b and S2 in the ESI † the SEM images showed a 1D morphology of materials. The average thickness of nanorods was calculated to be 42 ± 6 nm by measuring 159 samples (Fig. 2c).

The thickness and length of rods and overall shapes of organic networks varied, depending on the volume of THF. The largest surface area was obtained with 24 mL of THF among the screened conditions in this work (Fig. S1 in the ESI †). According to analysis of the N₂ sorption isotherm, the materials showed a 474 m² g⁻¹ surface area and microporosity with a 1.00 cm³ g⁻¹ total pore volume (Fig. 3a and the inset). PXRD studies (refer to Fig. 5c) showed amorphous character, which was commonly observed in MON materials in the literature.¹⁻⁷ Thermogravimetric analysis showed that the VH-MON is stable up to 140 °C (Fig. S3 in the ESI †). The light absorption behavior was studied by UV/visible reflectance spectroscopy (Fig. 3b). The reddish orange materials showed efficient absorption of visible light in the range of 400–530 nm and vivid emission at 542 nm by 420 nm excitation light. According to reflectance spectroscopy, the optical band-gap was estimated to be ~2.4 eV through a plot of (F(R)hv)² versus hv (based on Kubelka-Munk theory, F(R) = (1–R)²/2R).²³

The chemical components of the VH-MON were investigated by solid phase ¹³C NMR and IR absorption spectroscopy. As shown in Fig. 3c, the observed ¹³C peaks were well assigned to the aryl, double bonds and cyano groups, confirming the expected network structure. The peaks at 147 and 109 ppm were
assigned to carbons in double bonds with H and CN substituents, respectively. The shoulder peak at 118 ppm was assigned to carbon in CN groups. The existence of CN groups was clearly confirmed by the observation of the IR absorption peak at 2213 cm⁻¹ (Fig. 3d). Elemental analysis showed C: 84.43%, H: 4.88%, and N: 8.45% for the VH-MON, supporting the expected network (repeating unit of C₄₅H₂₇N₄, C: 86.65%, H: 4.36%, and N: 8.98%).

The HOMO and LUMO energy levels of the VH-MON were simulated by density functional theory (DFT) calculation (Fig. 4, S4 and S5 in the ESI†). Triphenylamine (TA-donor) and 2,2’-(biphenyl-4,4’-diyl)diacrylonitrile (BN-acceptor) were adopted as two representative components of MONs (Fig. 4a). From a molecular modeling aspect, the VH-MON can be constructed by repeating the π-conjugated connections between the TA-donor and the BN-acceptor. At first, we obtained the optimized structures of the TA-donor and BN-acceptor. Then, we designed model systems, M-1–5 by using those geometries (Fig. 4a). M-1–4 with an increasing number of TA-donors and BN-acceptors were designed to represent the extended molecular structures for a part of the VH-MON. M-5 represents a branched networking. Finally, the frontier molecular orbital energy levels were analyzed to suggest the HOMO and LUMO energy levels of the VH-MON.

The calculated HOMO and LUMO levels for the model compounds (TA-donor, BN-acceptor, and M-1–5) are shown in Fig. 4b and Table S1 in the ESI†. Interestingly, for all of the systems, the HOMO levels (−5.04 to −5.11 eV) of M-1–5 were calculated to be close to that of the TA-donor (−4.95 eV). On the other hand, the LUMO levels (−2.08–2.39 eV) are located near that of the BN-acceptor (−2.21 eV). In addition, the electron densities of HOMO and LUMO for all molecular systems are mostly distributed over TA-donor and BN-acceptor moieties, respectively (Fig. 4c and S4 in the ESI†). It implies that extended/branched networking through condensation reactions might not induce a significant change of the HOMO/LUMO energy levels for the VH-MON, compared with the HOMO and LUMO levels of the TA-donor and BN-acceptor, respectively. Thus, the HOMO and LUMO energy levels of the VH-MON can be predicted at −5.1 and −2.4 eV, respectively (Fig. 4b). Considering the location of conduction (−4.25 eV) and valence bands of TiO₂, the VH-MON can be used as light harvesting materials in combination with TiO₂–Pt systems. The HOMO energy level of triethanolamine (TEOA) was calculated to be −4.99 eV, indicating that the TEOA can serve as an electron sacrificial for the VH-MON (see Fig. S4 and S5 and Table S1 in the ESI†).

For the preparation of the VH-MON/TiO₂–Pt composite, the TiO₂–Pt powder was dispersed in methanol and treated with ultrasound. Then, the reaction mixture with the VH-MON was refluxed for 12 hours (see the Experimental section). According to transmission electron microscopy (TEM) analysis, the TiO₂–Pt was well dispersed over the VH-MON (Fig. 5a and b). The calculated HOMO and LUMO levels for the model compounds (TA-donor, BN-acceptor, and M-1–5) are shown in Fig. 4b and Table S1 in the ESI†. Interestingly, for all of the systems, the HOMO levels (−5.04 to −5.11 eV) of M-1–5 were calculated to be close to that of the TA-donor (−4.95 eV). On the other hand, the LUMO levels (−2.08–2.39 eV) are located near that of the BN-acceptor (−2.21 eV). In addition, the electron densities of HOMO and LUMO for all molecular systems are mostly distributed over TA-donor and BN-acceptor moieties, respectively (Fig. 4c and S4 in the ESI†). It implies that extended/branched networking through condensation reactions might not induce a significant change of the HOMO/LUMO energy levels for the VH-MON, compared with the HOMO and LUMO levels of the TA-donor and BN-acceptor, respectively. Thus, the HOMO and LUMO energy levels of the VH-MON can be predicted at −5.1 and −2.4 eV, respectively (Fig. 4b). Considering the location of conduction (−4.25 eV) and valence bands of TiO₂, the VH-MON can be used as light harvesting materials in combination with TiO₂–Pt systems. The HOMO energy level of triethanolamine (TEOA) was calculated to be −4.99 eV, indicating that the TEOA can serve as an electron sacrificial for the VH-MON (see Fig. S4 and S5 and Table S1 in the ESI†).

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surface area of the composite was reduced from 474 m² g⁻¹ (VH-MON) to 237 m² g⁻¹ due to the 50 wt% TiO₂-Pt content (surface area of 40 m² g⁻¹). PXRD confirmed the existence of TiO₂ materials in the composite (Fig. 5c).

Using the VH-MON/TiO₂-Pt composite (8 mg), its photocatalytic performance was studied in visible light-induced hydrogen production from water (see the Experimental section for details of the procedure). A 200 W Xe lamp with an optical filter (<420 nm cutoff) and a 4.6 mW cm⁻² intensity was used. The triethanolamine (10% TEOA, 3 mL) was used as an electron sacrifier. For comparison, single-molecular dye based systems such as eosin-Y/TiO₂-Pt and N719/TiO₂-Pt were prepared by the conventional adsorption procedure reported in the literature. Fig. 6 summarizes the results using the same amount (8 mg) of catalytic systems.

As indicated by the pink lines in Fig. 6, the eosin-Y/TiO₂-Pt system showed the highest external quantum efficiency with 82 μmol hydrogen production in the first 5 hours. However, it showed a sharp decrease with 12, 6 and 2 μmol hydrogen production in three successive tests (each of 5 hours), respectively. The external quantum yields for hydrogen production decreased sharply from 8.6% to 0.2% in four runs. The N719/TiO₂-Pt system showed more stable but less efficient performance with 43 μmol hydrogen production in the first 5 hours than the organic system of the eosin-Y/TiO₂-Pt system (blue lines in Fig. 6). However, it also showed a gradual decrease of performance with 26, 19 and 12 μmol hydrogen production, respectively, in the three successive tests (each of 5 hours), possibly due to the decomposition or detachment of dyes. The external quantum yields decreased from 4.5% to 1.3% in four runs. In comparison, the VH-MON/TiO₂-Pt system showed promising activity with 50 μmol hydrogen production in the first 5 hours and enhanced stability with 47, 52, 46, and 45 μmol hydrogen production (red lines in Fig. 6), respectively, in the four successive tests (each of 5 hours). The external quantum yield in the first run and the average value in the five runs were calculated to be 5.2% and 5.0%, respectively. Even in the fifth run, 4.7% quantum yield was maintained. The SEM images of the recovered composite showed nearly no change in the morphologies (Fig. S6 in the ESI†). The enhanced stability of the VH-MON/TiO₂-Pt system can be attributed to the crosslinking of light harvesting components which retards kinetically the decomposition pathways or blocks the leaching of light harvesting components into solution.

In conclusion, this work shows that visible light harvesting organic materials with a high surface area and microporosity can be prepared by crosslinking of electronic push and pull organic building blocks. The obtained photoactive and microporous organic network showed enhanced stability in visible light-induced hydrogen evolution from water. We believe that more efficient photocatalytic MON systems can be prepared through the synthetic screening of diverse photoactive chemical species.

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Notes and references


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20 When piperidine or DBU(1,8-diazabicycloundec-7-ene) was used as a base instead of NaOH, the solids were not obtained. When K2CO3 was used as a base instead of NaOH, the reaction resulted in the formation of irregular materials with a very poor yield. When toluene or dimethylformamide was used with NaOH as a solvent instead of THF, the reaction showed no conversion and a very poor yield, respectively. 
21 P. Kubelka and F. Munk, Zh. Tekh. Fiz., 1931, 12, 593. See Fig. S7 in the ESL. 
Unfortunately, water cannot be used as an electron donor in this system.


For comparison, the monomeric dye was also prepared by the reaction of tri(4-formylphenyl)amine with 3 eq. of cyanomethylbenzene. When the monomeric dye (4 mg) was used with TiO$_2$–Pt powder (4 mg) in photocatalytic reactions, the hydrogen production from water was not efficient (Fig. S8 in the ESI†).

Commercial bis(tetrabutylammonium) *cis*-di(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II), N719, was used.

See Table S2 in the ESI† for more details.