Supplementary Information

Mimicking 2, 2′:6′, 2″:6″, 2‴-Quaterpyridine Complexes for the Light-Driven Hydrogen Evolution Reaction: Synthesis, Structural, Thermal and Physicochemical Characterizations

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X-ray Crystallographic data
**Fig. S1.** Thermal atomic displacement ellipsoid plot of the structure of 12 grown from DMSO/EtOAc. The ellipsoids of non-hydrogen atoms are drawn at 50% probability level, and hydrogen atoms are represented by a sphere of arbitrary size.

**Fig. S2.** Thermal atomic displacement ellipsoid plot of the structure of 13 grown from DMSO/EtOAc. The ellipsoids of non-hydrogen atoms are drawn at 50% probability level, and hydrogen atoms are represented by a sphere of arbitrary size.
**Fig. S3.** Thermal atomic displacement ellipsoid plot of the structure of 14 grown from DMSO/THF.

The ellipsoids of non-hydrogen atoms are drawn at 50% probability level, and hydrogen atoms are represented by a sphere of arbitrary size.

**Table S1.** Hydrogen-bond geometry (Å, °) in structure of 12

| D—H···A     | D—H   | H···A | D···A   | D—H···A |
|-------------|-------|-------|---------|---------|
| O1—H1A···O2 | 0.88  | 2.46  | 3.165 (3)| 138     |
| O1—H1A···O4 | 0.88  | 1.93  | 2.789 (3)| 164     |
| O1—H1A···N7 | 0.88  | 2.55  | 3.403 (3)| 167     |
| O1—H1B···S1 | 0.88  | 2.94  | 3.6667 (18)| 142  |
| O1—H1B···O5 | 0.88  | 1.86  | 2.727 (3)| 167     |
| N5—H5A···N3i | 0.88 | 2.24  | 3.059 (3)| 156     |
| N5—H5B···O2 | 0.88  | 2.16  | 2.811 (3)| 131     |
| N6—H6A···O2i | 0.88 | 2.09  | 2.962 (3)| 173     |
| N6—H6B···O5i | 0.88 | 2.03  | 2.878 (3)| 162     |

Symmetry codes: (i) −x+1, −y+2, −z+1; (ii) −x+1, −y+1, −z+1.
Table S2. Hydrogen-bond geometry (\AA, °) in structure of 13

| D—H···A         | D—H  | H···A | D···A  | D—H···A |
|-----------------|------|-------|--------|---------|
| N11—H11A···O5  | 0.83 (4) | 2.17 (4) | 2.998 (3) | 172 (3) |
| N11—H11B···O5† | 0.88 (5) | 2.59 (4) | 3.180 (3) | 125 (3) |
| N11—H11B···O6† | 0.88 (5) | 2.19 (5) | 3.051 (3) | 165 (4) |
| N5—H5A···O2    | 0.85 (4) | 2.24 (4) | 2.957 (3) | 142 (3) |
| N5—H5A···N11   | 0.85 (4) | 2.54 (4) | 3.153 (3) | 129 (3) |
| N5—H5B···O9    | 0.79 (4) | 2.19 (4) | 2.954 (4) | 161 (4) |
| N6—H6A···O10   | 0.87 (4) | 2.06 (4) | 2.926 (3) | 173 (3) |
| N6—H6B···O4‡  | 0.81 (4) | 2.25 (4) | 3.040 (3) | 165 (4) |
| N12—H12A···O8  | 0.80 (4) | 2.11 (4) | 2.903 (4) | 170 (4) |
| N12—H12B···O7  | 0.79 (4) | 2.23 (4) | 2.994 (4) | 162 (4) |

Symmetry codes: (i) −x+1, −y+1, −z+1; (ii) −x, −y+1, −z+1.

Table S3. Hydrogen-bond geometry (\AA, °) in structure of 14

| D—H···A         | D—H  | H···A | D···A  | D—H···A |
|-----------------|------|-------|--------|---------|
| N5—H5A···O20A †| 0.88 | 2.01  | 2.822 (7) | 153 |
| N5—H5A···O20B †| 0.88 | 1.97  | 2.826 (16) | 163 |
| N5—H5B···O5    | 0.88 | 2.14  | 2.941 (4) | 151 |
| N6—H6A···O6‡  | 0.88 | 2.10  | 2.966 (4) | 169 |
| N6—H6B···N9‡  | 0.88 | 2.17  | 3.023 (4) | 163 |
| N11—H11A···N4 †| 0.88 | 2.25  | 3.129 (4) | 176 |
| N11—H11B···O3  | 0.88 | 2.25  | 2.972 (5) | 140 |
| N11—H11B···N5  | 0.88 | 2.56  | 3.130 (5) | 124 |
| N12—H12A···O4‡ | 0.88 | 2.12  | 2.936 (4) | 154 |
| N12—H12B···O21A‡| 0.88 | 1.96  | 2.800 (6) | 158 |

Symmetry codes: (i) −x+1/2, y−1/2, −z+3/2; (ii) x−1, y, z; (iii) −x+1/2, y+1/2, −z+3/2; (iv) −x+3/2, y−1/2, −z+3/2.
Thermal analysis

![Thermogravimetric analysis (TGA) curves of 6 and 12-14](image)

**Fig. S4.** Thermogravimetric analysis (TGA) curves of 6 and 12-14

Infrared spectroscopy

![Infrared spectra of 6 and 12-14](image)

**Fig. S5.** Infrared spectra of 6 and 12-14
**Table S4.** IR data and assignments of vibrations for ligand 6 and complexes 12-14

|   | ν/cm\(^{-1}\) | 6 | 12 | 13 | 14 | Assignment*** |
|---|---------------|---|----|----|----|---------------|
| 594w | 572w | 579w | 611w | τ (NO\(_3\)) |
| 621w | 625w | 623w | 625w | Triazine as well as bipyridine ring out-of-plane |
| 635w | 648w | 654w | 660w | deff. γ(C-N), γ(C-C) |
| 702w | 705vw | 705vw | 700w | Triazine ring out-of-plane def. γ(C-N), ω(NH\(_2\)) |
| 711sh | 729vw | 720w |  |  |
| 750w | 742vw | 745vw | 749w | ω(NH\(_2\)) |
| 761sh | 758w | 758w | 765w |  |
| 803m | 800m | 800s | 799m |  |
| 820sh | 817w | 815vw | 827w | Triazine ring out-of-plane def. γ(C-N), ω(C-H) |
| 843w | 832w | 831w |  |  |
| 914w | 917w | 917w | 912w |  |
|  | 927w |  |  | Ring breathing both triazine as well as bipyridine |
| 955vw | 955vw | 955vw | 951w |  |
| 989w | 991w | 987w | 981w |  |
| 1029w | 1032w |  |  |  |
| 1045w | 1044w | 1040w |  |  |
| 1077w | 1071w | 1074w |  |  |
| 1080w |  | 1083w |  |  |
| 1108s | 1136w | 1134w |  | Bipyridine ring breathing, ρ(NH\(_2\)), ρ(C-H) |
| 1157sh | 1165w | 1164w | 1163w | ω(NH\(_2\)), δ(C-H), ρ(NH\(_2\)) |
| 1198w | 1203w | 1201w | 1201w | Triazine ring def., τ(NH\(_2\)) |
| 1254w | 1276m | 1284m | 1270w |  |
| 1275w | 1313s | 1313s | 1323s | ν(C-N) aromatic amines |
| 1370w | 1390s | 1388s | 1371m | ρ(C-H) |
| 1401m |  |  |  |  |
| 1439m | 1423s | 1418s | 1417w |  |
| 1456w | 1454sh | 1470w | 1470w | ρ(C-H) |
| 1482w | 1481w | 1480w |  |  |
| 1537s | 1525s | 1523s | 1513s | Bipyridine ring breathing ν(C-C), δ(NH\(_2\)) |
| 1567m | 1568m | 1574m |  | δ(NH\(_2\)) |
| 1591w | 1588w | 1590m |  |  |
| 1618s | 1617s | 1616s | 1609w | Triazine ring breathing ν(C-N), δ(NH\(_2\)) |
| 1657w | 1661m | 1658w | 1655w | Triazine ring breathing ν(C-N) |
|  | 1668m |  |  |  |
| 3084w | 3083w | 3085w | 3066sh | ν(C-H) |
| 3137s | 3099w | 3100w |  |  |
| 3178s | 3165sh | 3185w | 3154sh | ν\(_2\)(NH\(_2\)) |
| 3312s | 3219m | 3230s | 3214s | ν\(_2\)(NH\(_2\)) |
| 3405w | 3383s | 3340s | 3316s | ν\(_2\)(NH\(_2\)), ν\(_3\)(NH\(_2\)) |
| 3487m | 3436m | 3458s | 3420m |  |

***Abbreviation used for the type of vibration mode. deff.: deformation; δ, γ, ρ, τ, ω: bending vibrations; ν: stretching vibration
Cyclic Voltammetry

**Fig. S6.** Cyclic voltammetry of 6, 12 and 13 in full scale

**Table S5.** Cyclic voltammetry data of 2, 2′:6′, 2″-quaterpyridine complexes reported in literature

| Compound                      | Solvent | Eox1/2 [V] | Ered1/2 [V] | Ered2/1/2 [V] | Ered3/2 [V] | Ered4/2 [V] |
|-------------------------------|---------|------------|-------------|---------------|-------------|-------------|
| Co(qtpy)(H$_2$O)$_2$(ClO$_4$)$_2$ | MeCN    | -0.65      | -1.15       | ---           | ---         | ---         |
| Ni(qtpy)(ClO$_4$)$_2$         | DMF     | -0.79      | -1.13       | -1.90         | ---         | ---         |
| Cu(qtpy)(PF$_6$)$_2$          | MeCN    | 0.13 (nr)  | -0.24 (nr)  | ---           | ---         | ---         |

qtpy = 2, 2′:6′, 2″-quaterpyridine, nr = non-reversible
**Fig. S7** Emission spectrum of blue LED.

**Table S6.** Emission maxima and amplitude of LED light.

| Light source | Blue |
|--------------|------|
| $\lambda_{\text{max,em}}$ (nm) | 445 |
| $\Delta \lambda$ (nm) | 90 |
| Photon flux in $\mu$mol$_{\text{photons}}$.min$^{-1}$.cm$^{-2}$ | 20 |

*a* blue LED 445 nm.

*b* an analog power-meter PM100A (THORLABS) associated with a compact photodiode power head with silicon detector S120C is used to evaluate the photon flux for the LEDs. Photo-diode detector is placed at the same distance from the LED surface than the bottom of illuminated vial.

**HER Curves of Co(II), Ni(II) and Cu(II) nitrates**

**Fig. S8.** Hydrogen evolution reaction of Co(NO$_3$)$_2$. 6H$_2$O, Ni(NO$_3$)$_2$. 6H$_2$O and Cu(NO$_3$)$_2$. 2.5H$_2$O (1 mM each) under blue light. (a) TON’s and (b) TOF’s.
**Mechanism of hydrogen evolution reactions**

The mechanism of the hydrogen evolution reaction may occur by two important steps; (I) Activation of the molecular catalyst by the photosensitizer and (II) Redox photocatalytic hydrogen evolution.

**Step I**

**A**

\[
\text{hv} \quad \text{Ru}(II) \quad \text{Ru}(II)^* \quad \text{D} \quad \text{D}^+ \quad \text{M}(I) \quad \text{M}(II) \quad \text{Reductive Quenching}
\]

**B**

\[
\text{hv} \quad \text{Ru}(II) \quad \text{Ru}(II)^* \quad \text{M}(II) \quad \text{M}(I) \quad \text{Oxidative Quenching}
\]

**Fig. S9.** Photosensitizer based processes in light-driven hydrogen evolution reaction

In step I, activation of the molecular photocatalyst can take place either by reductive or oxidative quenching pathways from the excited photosensitizer (PS*). Visible light is used to for the excitation of the photosensitizer where, in the process of reductive quenching (A), the excited PS* accept an electron from the sacrificial electron donor (SED) and shares it with the molecular catalyst, during this course, the oxidation state of Ru(II) does not change. In the process of oxidative quenching (B), the excited PS* oxidizes and donates its electron to the molecular catalysts and then abstracts an electron from the SED, this process involves redox changes in Ru(II) PS.

In step II, at the photocatalytic centre, the hydrogen evolution can occur by two different mechanisms.
Step II

Fig. S10. Heterolytic and homolytic mechanisms of hydrogen evolution reaction catalysed by molecular photocatalyst

In heterolytic mechanism (C), H₂ is evolved by the protonation of the intermediate metal hydride. In the catalytic cycle, the two electrons are transferred either consecutively or alternatively. The H₂ evolution in the alternative homolytic pathway (D) happens by the reductive elimination of two metal hydride intermediates. In both the mechanisms, the metal salts of +II oxidation state undergoes one electron reduction before protonation takes place.³

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