

## Supporting Information for

### **Role of the excited state hydrogen bonding in CO<sub>2</sub> photoreduction catalyzed by sodium magnesium chlorophyll**

Naitian Zhang, Yuehui Li, Wenzhe Shang, Xuedan Song, Wei Liu, Ce Hao\*

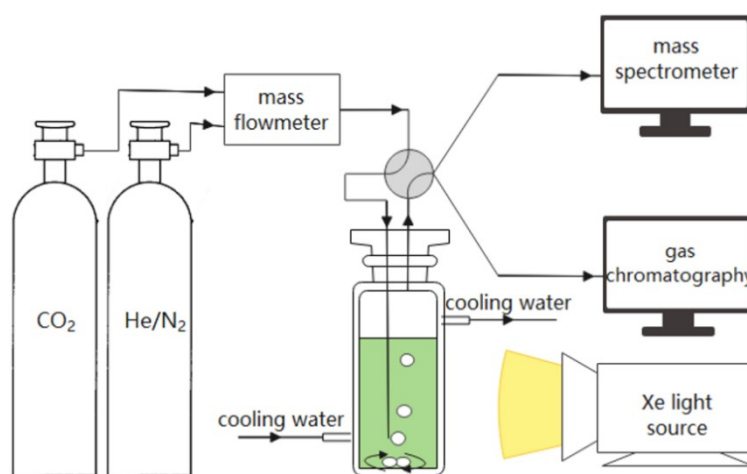
**Affiliations:**

*State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian  
University of Technology, Dalian, 116024, China*

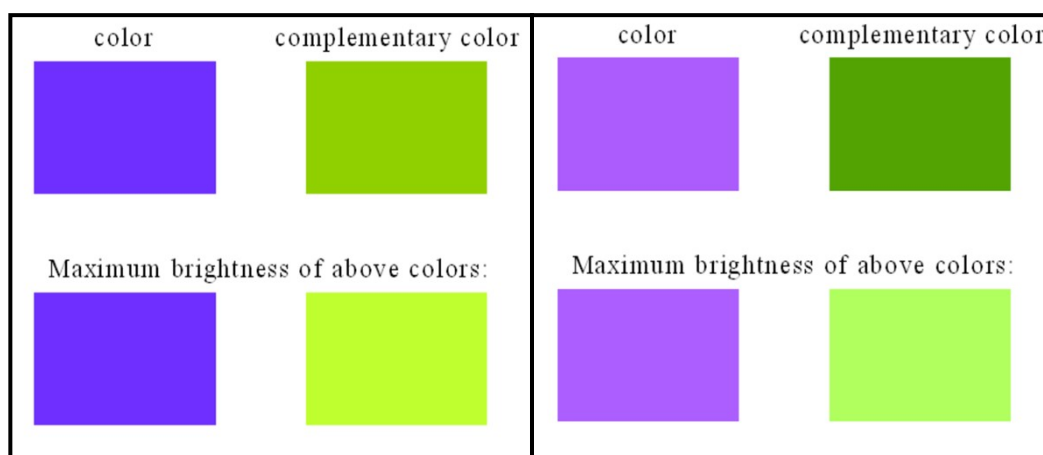
Corresponding authors: *E-mail address: haoce@dlut.edu.cn (C. Hao)*

## Supplement of experimental facility and details

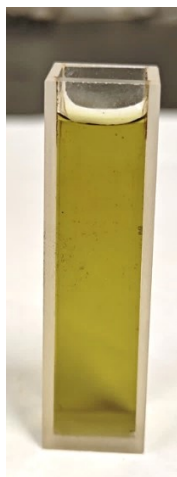
For the gas chromatography (GC) measurements, the  $\text{CO}_2/\text{N}_2$  is used as the equilibrium gas fed into the home-made quartz reactor from a cylinder via a mass flow meter until the solution is saturated. For the mass spectrometry (MS) characterization, He and  $\text{CO}_2/^{13}\text{CO}_2$  are used in the carrier gases fed into the home-made quartz reactor. Afterwards, the four-way valve is closed, and the gas products were detected by the gas chromatography or mass spectrometry after the illumination. The schematic diagram of the reaction device is shown in Fig. S1.



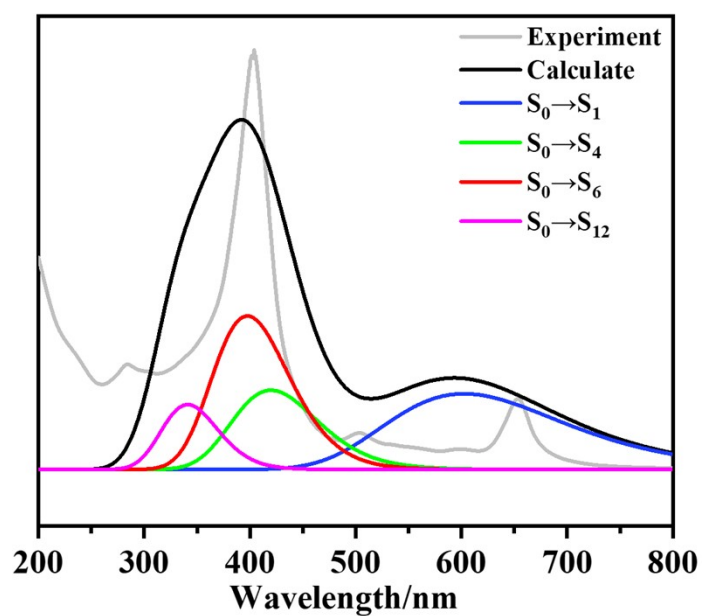
**Fig. S1** Schematic diagram of photocatalytic reaction device.



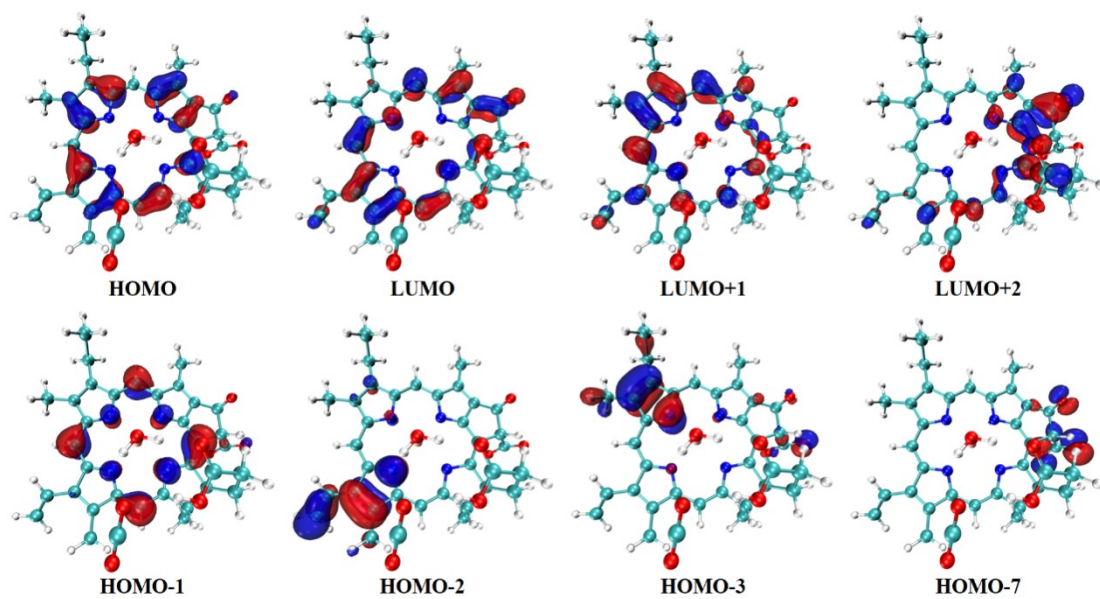
**Fig. S2** The left side displays the experimental measured ultraviolet-visible spectrum with its predicted absorption colors and their complementary colors, while the right side shows the theoretically computed ultraviolet-visible spectrum with its predicted absorption colors and their complementary colors.



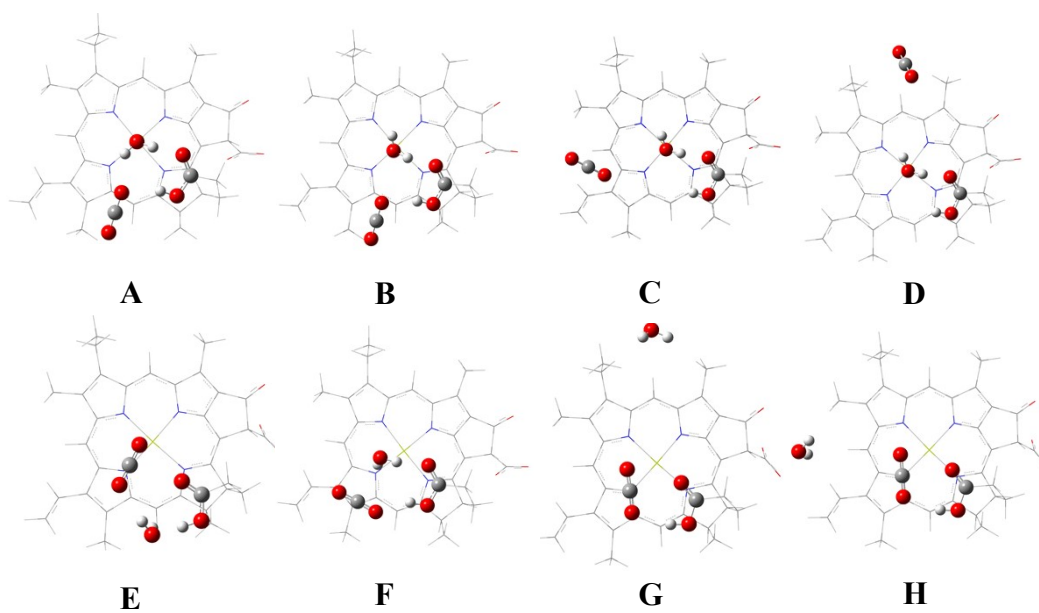
**Fig. S3** The color of  $\text{MgChlNa}_2$  dissolved in water.



**Fig. S4** The UV-visible spectrum of  $\text{MgChlNa}_2$  is compared with the corresponding calculated UV-visible spectrum, along with the individual excited states contributions.



**Fig. S5** The molecular orbital isosurfaces mentioned in Table S1, the positive and negative phase of the orbital wave function are shown in red and blue, respectively.

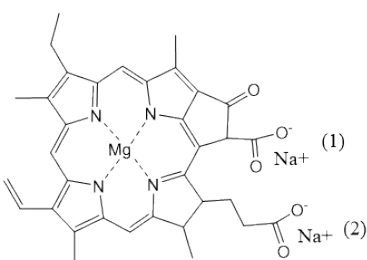


**Fig. S6** Structural models of different hydrogen bonding complexes.

**Table S1** Orbital component contributions for  $S_0 \rightarrow S_1$ ,  $S_0 \rightarrow S_4$  and  $S_0 \rightarrow S_6$ 

	nm	oscillator strength			Contribute
$S_0 \rightarrow S_1$	602.3	0.33	HOMO	LUMO	88.47%
			HOMO-1	LUMO+1	10.69%
$S_0 \rightarrow S_4$	420.0	0.35	HOMO	LUMO+1	56.21%
			HOMO-3	LUMO	11.17%
$S_0 \rightarrow S_6$	397.6	0.67	HOMO-1	LUMO+1	49.43%
			HOMO-3	LUMO	16.13%
			HOMO	LUMO+1	12.15%
$S_0 \rightarrow S_{12}$	341.2	0.28	HOMO-1	LUMO+2	59.07%
			HOMO-7	LUMO	11.72%
			HOMO-2	LUMO+1	10.36%

**Table S2** Energy comparison of the system after protonation of the two different carboxyl groups in the system.

	Relative energy (kcal/mol)	
	Site (1)	
Site (2)		0

The carboxyl group at site (2) has the lowest energy after protonation, so the carboxyl group at site (2) has first priority of hydrolysis.

**Table S3** The relative energies of the different hydrogen-bonded complexes

Structures	Relative energies (kal/mol)
A	0
B	1.0
C	2.8
D	3.4
E	5.1
F	8.3
G	12.8
H	13.2

**The reaction order is derived as follows:**

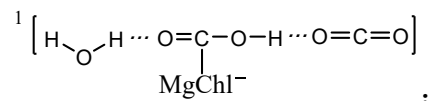
The total reaction rate is determined by the rate of the rate-limiting step:

$$r = -dc \left( {}^1 \left[ \text{H}_2\text{O} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}=\text{C}=\text{O} \right]^* \right) / dt = k_3 c \left( {}^1 \left[ \text{H}_2\text{O} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}=\text{C}=\text{O} \right]^* \right) \quad (1)$$

For the absorption equilibrium formed by CO<sub>2</sub>, H<sub>2</sub>O and the catalyst:

$$K_1 = c \left( {}^1 \left[ \text{H}_2\text{O} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}=\text{C}=\text{O} \right] \right) / c(\text{CO}_2)c(\text{H}_2\text{O})c(\text{MgChlH}^-) \quad (2)$$

For the equilibrium between  ${}^1 \left[ \text{H}_2\text{O} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}=\text{C}=\text{O} \right]^*$  And



$$K_2 = c \left( {}^1 \left[ \text{H}_2\text{O} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}=\text{C}=\text{O} \right]^* \right) / c \left( {}^1 \left[ \text{H}_2\text{O} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}=\text{C}=\text{O} \right] \right)$$

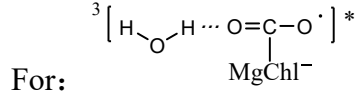
Then,

$$c \left( {}^1 \left[ \text{H}_2\text{O} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}=\text{C}=\text{O} \right]^* \right) = K_1 K_2 c(\text{CO}_2)c(\text{H}_2\text{O})c(\text{MgChlH}^-)$$

$$(3) \quad {}^3 \left[ \text{H}_2\text{O} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}=\text{C}=\text{O} \right]^* \quad \text{For :}$$

$$dc \left( {}^3 \left[ \text{H}_2\text{O} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}=\text{C}=\text{O} \right]^* \right) / dt = k_4 c \left( {}^3 \left[ \text{H}_2\text{O} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}=\text{C}=\text{O} \right]^* \right) - k_3 c \left( {}^1 \left[ \text{H}_2\text{O} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}=\text{C}=\text{O} \right]^* \right) = 0$$

$$k_3 c \left( {}^1 \left[ \text{H}_2\text{O} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}=\text{C}=\text{O} \right]^* \right) = k_4 c \left( {}^3 \left[ \text{H}_2\text{O} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}=\text{C}=\text{O} \right]^* \right) \quad (4)$$



$$dc \left( {}^3 \left[ \text{H}-\text{O}-\text{H} \cdots \text{O}=\text{C}-\text{O} \cdot \right]^*_{\text{MgChl}^-} \right) / dt = k_4 c \left( {}^3 \left[ \text{H}-\text{O}-\text{H} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}=\text{C}=\text{O} \right]^*_{\text{MgChl}^-} \right) - k_5 c \left( {}^3 \left[ \text{H}-\text{O}-\text{H} \cdots \text{O}=\text{C}-\text{O} \cdot \right]^*_{\text{MgChl}^-} \right) = 0$$

Then 
$$k_4 c \left( {}^3 \left[ \text{H}-\text{O}-\text{H} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}=\text{C}=\text{O} \right]^*_{\text{MgChl}^-} \right) = k_5 c \left( {}^3 \left[ \text{H}-\text{O}-\text{H} \cdots \text{O}=\text{C}-\text{O} \cdot \right]^*_{\text{MgChl}^-} \right) \quad (5)$$

For  $\dot{\text{COOH}}$  in(4):

$$dc(\dot{\text{COOH}}) / dt = k_4 c \left( {}^3 \left[ \text{H}-\text{O}-\text{H} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}=\text{C}=\text{O} \right]^*_{\text{MgChl}^-} \right) - k_6 c(\text{COOH})c(\text{OH}) + k_{-6} c(\text{CO})c^2(\text{OH}) \quad (6)$$

For  $\dot{\text{OH}}$  in(5):

$$dc(\dot{\text{OH}}) / dt = k_5 c \left( {}^3 \left[ \text{H}-\text{O}-\text{H} \cdots \text{O}=\text{C}-\text{O} \cdot \right]^*_{\text{MgChl}^-} \right) - k_6 c(\dot{\text{COOH}})c(\dot{\text{OH}}) + k_{-6} c(\text{CO})c^2(\dot{\text{OH}}) \quad (7)$$

$K_6$  in(6):

$$K_6 = c(\text{CO})c^2(\dot{\text{OH}}) / c(\dot{\text{COOH}})c(\dot{\text{OH}}) = c(\text{CO})c(\dot{\text{OH}}) / c(\dot{\text{COOH}})$$

$$c(\dot{\text{COOH}})c(\dot{\text{OH}}) = c(\text{CO})c^2(\dot{\text{OH}}) / K_6 \quad (8)$$

Substitute (8) into (6):

$$dc(\dot{\text{COOH}}) / dt = k_4 c \left( {}^3 \left[ \text{H}-\text{O}-\text{H} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}=\text{C}=\text{O} \right]^*_{\text{MgChl}^-} \right) - (k_6 / K_6 - k_{-6}) c(\text{CO})c^2(\dot{\text{OH}}) = 0 \quad (9)$$

Form(4)(5)(9):

$$\begin{aligned} k_3 c \left( {}^1 \left[ \text{H}-\text{O}-\text{H} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}=\text{C}=\text{O} \right]^*_{\text{MgChl}^-} \right) &= k_4 c \left( {}^3 \left[ \text{H}-\text{O}-\text{H} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}=\text{C}=\text{O} \right]^*_{\text{MgChl}^-} \right) \\ &= k_5 c \left( {}^3 \left[ \text{H}-\text{O}-\text{H} \cdots \text{O}=\text{C}-\text{O} \cdot \right]^*_{\text{MgChl}^-} \right) = (k_6 / K_6 - k_{-6}) c(\text{CO})c^2(\dot{\text{OH}}) \end{aligned} \quad (10)$$

Form(3):

$$-dc \left( {}^1 \left[ \text{H}-\text{O}-\text{H} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}=\text{C}=\text{O} \right]^*_{\text{MgChl}^-} \right) / dt = -dc \left( {}^1 \left[ \text{H}-\text{O}-\text{H} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}=\text{C}=\text{O} \right]^*_{\text{MgChl}^-} \right) K_2 / dt$$

$$= -dK_1 K_2 c(\text{CO}_2)c(\text{H}_2\text{O})c(\text{MgChlH}^-) / dt = -K_1 K_2 c(\text{MgChlH}^-)c(\text{H}_2\text{O})d\text{CO}_2 / dt = (k_6 / K_6 - k_{-6}) c(\text{CO})c^2(\dot{\text{OH}})$$

For(  $\text{H}_2\text{O}_2$ ):

$$dc(\text{H}_2\text{O}_2)/dt = k_7 c^2(\dot{\text{O}}\text{H}) - k_8 c(\text{H}_2\text{O}_2) + k_{-8} c^{1/2}(\text{O}_2) c(\text{H}_2\text{O}) = 0$$

$$k_7 c^2(\dot{\text{O}}\text{H}) = k_8 c(\text{H}_2\text{O}_2) - k_{-8} c^{1/2}(\text{O}_2) c(\text{H}_2\text{O})$$

$$K_8 = c^{1/2}(\text{O}_2) c(\text{H}_2\text{O}) / c(\text{H}_2\text{O}_2)$$

$$c(\text{H}_2\text{O}_2) = c^{1/2}(\text{O}_2) c(\text{H}_2\text{O}) / K_8$$

$$k_7 c^2(\dot{\text{O}}\text{H}) = (k_8 / K_8 - k_{-8}) c^{1/2}(\text{O}_2) c(\text{H}_2\text{O})$$

$$c^2(\dot{\text{O}}\text{H}) = 1/k_7 (k_8 / K_8 - k_{-8}) c^{1/2}(\text{O}_2) c(\text{H}_2\text{O}) \quad (11)$$

Substitute(3)(10)(11)into(1)

$$-K_1 K_2 c(\text{MgChlH}^-) c(\text{H}_2\text{O}) d\text{CO}_2/dt = (k_6 / K_6 - k_{-6}) c(\text{CO}) c^2(\dot{\text{O}}\text{H})$$

$$= 1/k_7 (k_6 / K_6 - k_{-6}) (k_8 / K_8 - k_{-8}) c^{1/2}(\text{O}_2) c(\text{H}_2\text{O}) c(\text{CO})$$

$$-d(\text{CO}_2)/dt = [c^{1/2}(\text{O}_2) c(\text{H}_2\text{O}) c(\text{CO}) / K_1 K_2 c(\text{MgChlH}^-) c(\text{H}_2\text{O}) k_7] (k_6 / K_6 - k_{-6}) (k_8 / K_8 - k_{-8})$$

The concentration of the catalyst is constant,

$$-d(\text{CO}_2)/dt = k' c(\text{CO}) c^{1/2}(\text{O}_2).$$

The CO<sub>2</sub>RR is a first order reaction for the product CO.