

# Photoelectrochemical Behavior of Polychelate Porphyrin Chromophores and Titanium Dioxide Nanotube Arrays for Dye-Sensitized Solar Cells

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## Supporting Information

For **P2** (Figure S1), the  $\nu(\text{C}=\text{O})$  mode at  $1638\text{ cm}^{-1}$  is clearly seen in the Raman spectrum of species in solution and appears as a shoulder in the high frequency side tail of a larger band at  $1589\text{ cm}^{-1}$  due to the phenyl ring stretching modes.<sup>1</sup> This band shifts toward higher frequencies and appears at  $1657\text{ cm}^{-1}$  upon adsorption. Interestingly, its intensity decreases significantly but does not disappear as expected for a full coordination saturation of all carboxylic groups on the  $\text{TiO}_2$  NTA surface. The incomplete disappearance points out to the presence of some free carboxylic groups either because **P2** is coordinated to  $\text{TiO}_2$  only through one carboxylic group or because there are some porphyrin molecules trapped in the nanotubes and not directly bound to the surface. On the other hand, as expected upon adsorption, the symmetric stretching mode ( $\nu_s(\text{CO}_2^-)$ ) is at  $1417\text{ cm}^{-1}$  for solution species and appears broader and smaller upon binding to the  $\text{TiO}_2$  NTA surface.

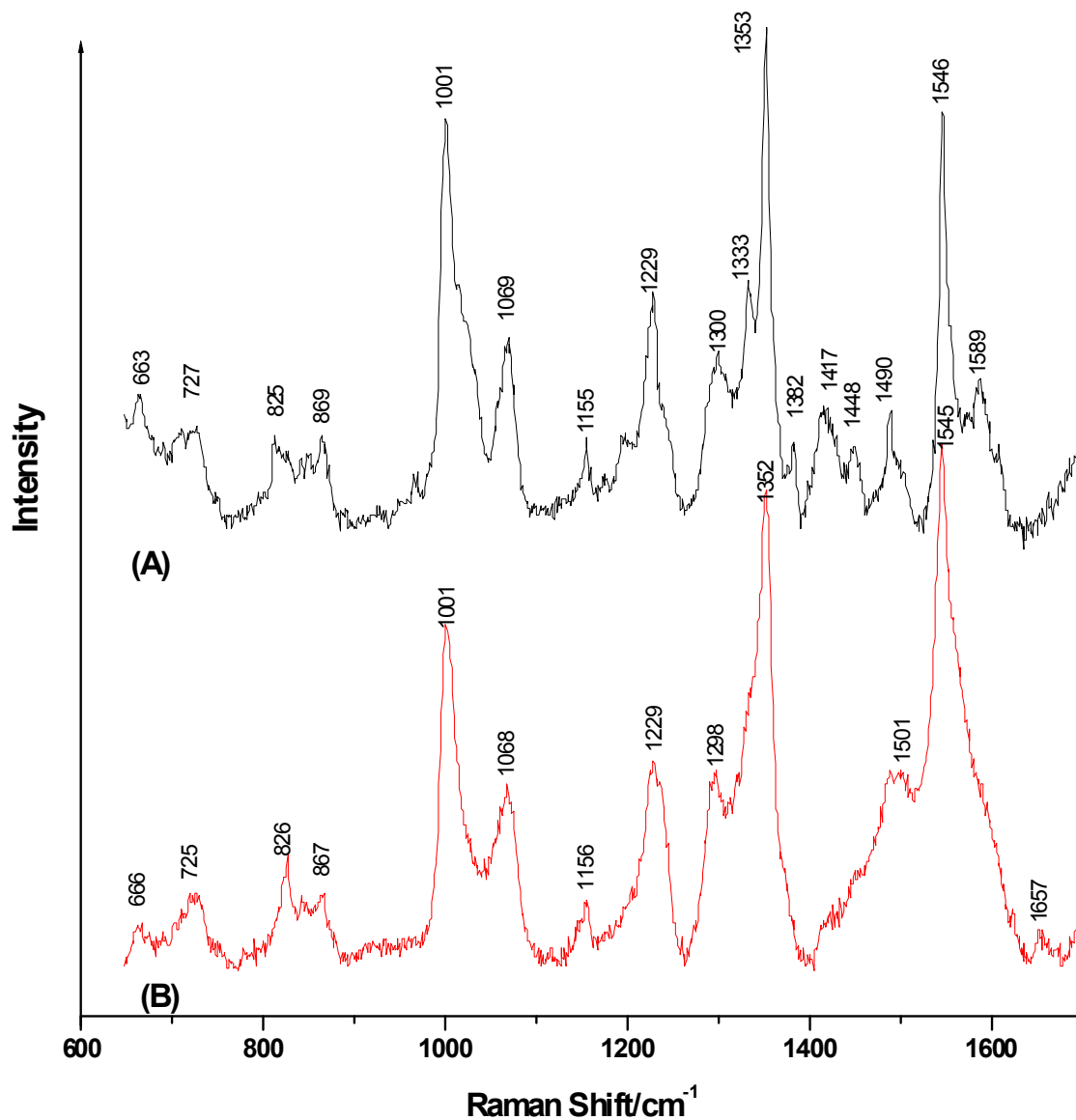
For **P2**, it is worth noting the  $\delta_s(\text{CO}_2^-)$  band at  $825\text{ cm}^{-1}$  is clearly less intense in the bound condition (where it is located at  $827\text{ cm}^{-1}$ ) than in the solution state while the wagging  $\omega(\text{OCO})$  mode is shifted from  $663$  to  $666\text{ cm}^{-1}$  for the adsorbed dye and decreases in intensity. Also the band at  $1300\text{ cm}^{-1}$  associated with  $\nu(\text{C}-\text{O})$  mode moves to  $1298\text{ cm}^{-1}$  upon adsorption but its

intensity does not seem to decrease as expected if all the carboxylic groups were attached to the TiO<sub>2</sub> surface. This may be diagnostic of significant porphyrin-porphyrin ring interaction resulting from aggregation (ring stacking) of the porphyrin groups (see above).<sup>2</sup> Our diffuse reflectance data obtained under the same conditions as the Raman spectra (Figure 2) does show some degree of aggregation for the **P2** compound.

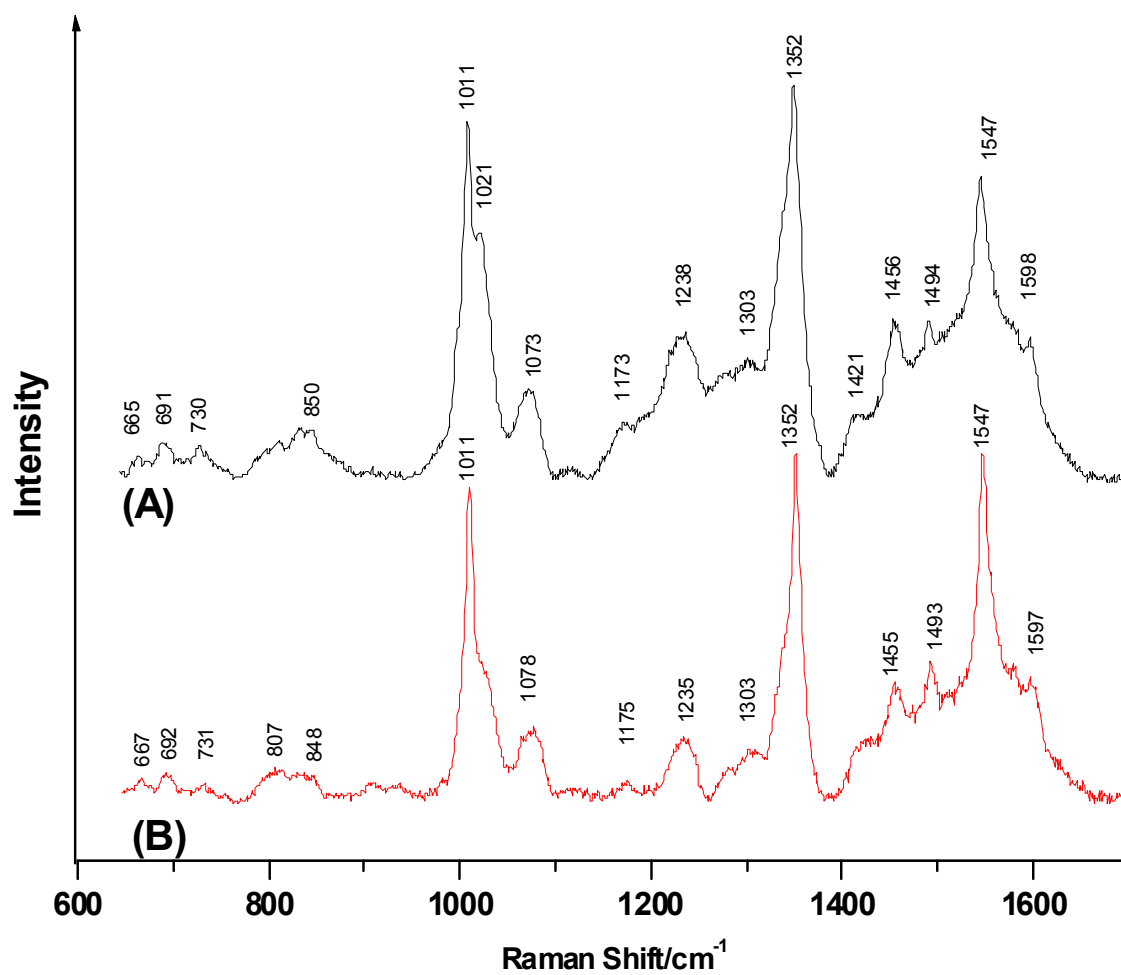
The Raman spectra of **P3** (Figure S2), both in solution and bound to TiO<sub>2</sub> NTA are less structured than those for the **P1** and **P2** porphyrins. The  $\nu_s(\text{OCO})$  feature at 1421 cm<sup>-1</sup> is seen in both conditions probably because some free carboxylic acid groups are still present in the bound situation. As in the **P2** case above, it is also likely that there are some porphyrin molecules not directly bound to the TiO<sub>2</sub> nanotube walls but are trapped inside the nanotubes. The symmetric ( $\text{CO}_2^-$ ) bending mode at 850 cm<sup>-1</sup> ( $\delta_s(\text{CO}_2^-)$ ) in solution is clearly less intense in the bound condition and shifted to 848 cm<sup>-1</sup>. Importantly, the  $\nu_a(\text{CO}_2^-)$  at 1547 cm<sup>-1</sup> is enhanced by binding while the bending  $\delta_a(\text{CO}_2^-)$  at 730 cm<sup>-1</sup> almost disappears upon binding.

The Raman spectra of **P4** (Figure S3) shares similarities with those of **P2** both in solution and in the adsorbed state. The band located at 1546-1550 cm<sup>-1</sup> assigned to  $\nu_a(\text{CO}_2^-)$  is relatively broader and with a more noticeable shoulder at 1599 cm<sup>-1</sup> for **P4** than for **P2** (c.f., Figures S3 and S1). These changes seem to be due to the electron-donating contribution of the methyl groups that **P2** has in the attached phenyl groups to the porphyrin ring (see Figure 1). The Raman spectra of **P5** (Figure S4) have similarities with those of **P3**. The 1303-1305 cm<sup>-1</sup> band associated with  $\nu(\text{C-O})$  stretching is more intense in **P5** than in **P3** in both solution and adsorbed states. For **P1**, **P3** and **P5**, a broad band at 1417-1420 cm<sup>-1</sup>, related to the  $\nu_s(\text{CO}_2^-)$  mode, increases in intensity upon adsorption while this effect was not observed in **P2** and **P4**.

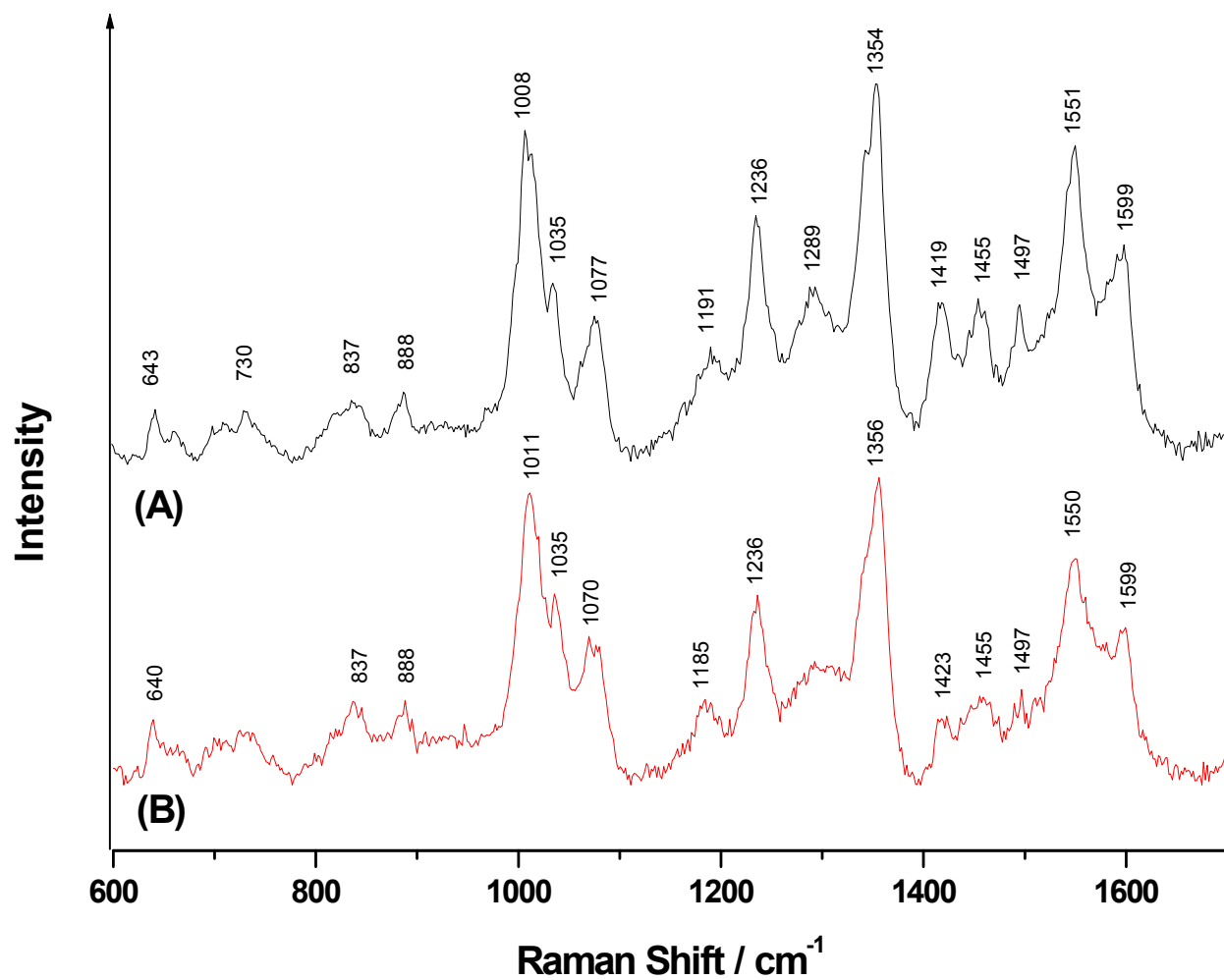
- (1) Cinta, S.; Venter, M.; Fickert, C.; Haiduc, I.; Scholz, P.; Kiefer, W. *J. Mol. Struct.* **1998**, *446*, 209.
- (2) Cherian, S.; Wamser, C. *J. Phys. Chem. B* **2000**, *104*, 3624.



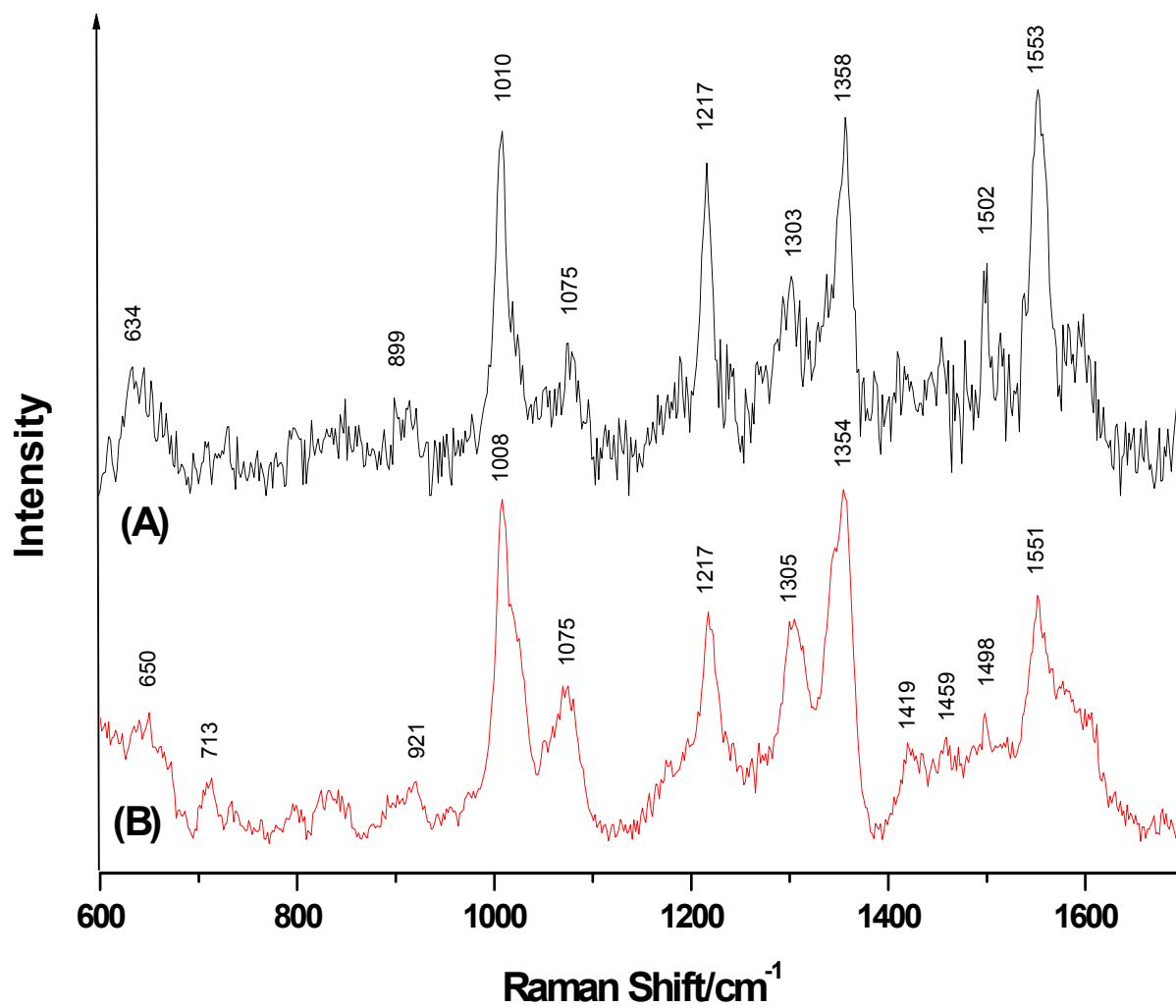
**Figure S1.** Resonance Raman spectra of compound **P2** dissolved in methanol (A) and bound to TiO<sub>2</sub> NTA (B). The TiO<sub>2</sub> NTA film used for this spectrum has an average inner diameter of 120 nm and was prepared by anodization at 20 V, 3 h with polyethylene glycol 400 (PEG 400) as medium modifier, and with a PEG 400:H<sub>2</sub>O ratio of 80:20.



**Figure S2.** Resonance Raman spectra of compound **P3** dissolved in methanol (A) and bound to TiO<sub>2</sub> NTA (B). Other details as in Figure S1.



**Figure S3.** Resonance Raman spectra of compound **P4** dissolved in methanol (A) and bound to TiO<sub>2</sub> NTA (B). Other details as in Figure S1.



**Figure S4.** Resonance Raman spectra of compound **P5** dissolved in methanol (A) and bound to TiO<sub>2</sub> NTA (B). Other details as in Figure S1.