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To cite this article: N A Rahim et al 2019 J. Phys.: Conf. Ser. 1156 012010

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Study of interaction of CoPcF₁₆ within poly 4-vinylpyridine matrix using UV/Vis spectroscopy

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Abstract. Metallophthalocyanine (MPc) complexes based on abundant transition metals has greatly interest as catalyst due to their attractive features including a rich redox behaviour, the potential to bind with metals or non-metals in the central cavity. Among the transiton metal, cobalt complexes as electrocatalyst are preferable due to their efficient catalytic activity. Immobilisation of the catalyst onto surface may improve with the poly 4-vinylpyridine (P4VP) as polymer backbone. However, aggreagation of MPc is the challenge to overcome. This study aims to investigate the interaction behaviour of cobalt(II) hexadecfluorophthalocyanine (CoPcF₁₆) within poly 4-inylpyridine (P4VP) using UV/Vis spectroscopy. Two solutions of CoPcF₁₆ and P4VP were mixed and the interaction of CoPcF₁₆-P4VP was observed through the time using UV/Vis spectroscopy at wavelength 500 to 750 nm. The outcome suggests that coordination of the electrocatalysts is favoured by the comportment of a high concentration of 4VP. Subsequently, this $CoPcF_{16}$ -P4VP electrocatalyst has a potential for water splitting or hydrogen evolution.

1. Introduction

Metallophthalocyanine (MPc) complexes have greater attention among the researchers because of their attractive characteristics such as a rich redox behavior complexes, accessible to change the ring by substitution, possible to bind with metals or non-metals in the central cavity and chemically stable [1]. MPcs are used as dyes in the paper and textile industry, photoconductors in photocopy machines [2], heavy metals sensors [3] and catalyst for water splitting [4-5]. MPcs and other similar compounds are employed as a promising catalyst for many reactions in the electrochemical area [6]. Cobalt complexes such as cobaloximes, diimine-dioximes, porphyrins and phthalocyanines were studied electrocatalysts and photocatalysts in water splitting or hydrogen evolution [5].

MPc coordination to ligands such as polyvinyl pyridine is forced by the presence of free radical coordination sites in nitrogen atom position. Cobalt phthalocyanine may be coordinated to either single or two pyridine units as has been recognised for other metal complexes [7]. This reaction is favoured because single molecule is predicted to be more effective as electrocatalyst than large aggregate. Many studies on aggregation and coordination of ligands at the axial position have been reported in 1980-1990s, however, the results reported are often ambiguous and questionable. In this study, the effect of

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IOP Conf. Series: Journal of Physics: Conf. Series 1156 (2019) 012010 doi:10.1088/1742-6596/1156/1/012010

incorporating $CoPcF_{16}$ with the polymer in different rations, aggregation and coordination were investigated through time by UV/Vis spectroscopy.

2. Materials and methods

All solvents were used directly as received and HPLC grade or better. Cobalt(II) hexadecafluorophthalocyanine (CoPcF₁₆) was purchased from Aldrich and poly 4-vinylpyridine (P4VP) 160,000 g/mol from Merck.

2.1 UV/Vis spectroscopy study

 $CoPcF_{16}$ (0.03 mM) and P4VP (0.045 mM) were prepared in dimethylformamide (DMF) solution. Both solutions were mixed at different ratios with maximum volume, 5 mL. The interaction between $CoPcF_{16}$ -P4VP was observed by UV/Vis spectroscopy via time at wavelength 500-750 nm. The details conditions of the experiments were demonstrated in table 1.

Table 1. Concentration of solvent mixtures $CoPcF_{16}$ -P4VP matrix at different ratios with total volume, 5 mL.

0.045 mM P4VP (mL)	0.03 mM CoPcF ₁₆ (mL)	Concentration P4VP (mM) ^a	Concentration CoPcF ₁₆ (mM) ^a
0	5	0	0.030
1	4	0.009	0.024
2	3	0.018	0.018
3	2	0.027	0.012
4	1	0.036	0.006

^a Concentration after mixing the solution was determined using equation $M_1V_1 = M_2V_2$ (M_1 = the stock concentration P4VP or CoPcF₁₆, V_1 = volume of P4VP or CoPcF₁₆ taken from the stock solution, M_2 = diluted concentration, V_2 = total volume after mixed the solution.

3. Results and discussion

The UV/Vis spectra showed the π - π^* band transitions within the macrocyclic phthalocyanine ring system (650-750 nm). For CoPcF₁₆ in DMF solution, homogeneously blue colour was discovered and two bands obtained in UV/Vis spectra of CoPcF16. The peaks are 628 nm and 448 nm indicating Q band and B band, respectively. Figure 1 and table 2 shows the UV/Vis spectra of CoPcF₁₆ and CoPcF₁₆/P4VP in DMF solution at different molecular ratios. The results showed a bathochromic shift with the low concentration of CoPcF₁₆ after 30 days. Therefore, the colour solution changes from blue to green. This may be a consequence of the formation of dimers and aggregation of the monomeric species [8] or coordination between P4VP and the Co centre [9]. The lowest concentration of CoPcF₁₆ (0.006 mM) contains an excess pyridine group (0.036 mM) availables for coordinating with MPc. Similar UV/Vis spectra results obtained from the film of CuPcF₁₆ in DMF solutions and aggregation formed at higher concentration [10].

In the interaction of MPc/polymer matrix, two possible chemical reactions ought to be brought into consideration which are the coordination of MPc to the polymer chains and the aggregation of MPc molecules in solution. Aggregation of MPcs is an extensively suggested characteristics of the compounds due to their significant π - π stacking. Electronic spectra in solution and films is depending on the substitution of phthalocyanine at α -, β - or hexadeca positions. Ogata *et al.* (2003) reported the MPC's interaction as follows (i) cofacial aggregation at α - position is impossible to occur, resulting the Q band appears at the same wavelength in solution or film; (ii) cofacial aggregation at β - position exists in polar solvent performing a broad Q band in the film; (iii) hexadeca substituted the compound exhibiting Q bands at the same wavelength in solution and film [11].

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Table 2. Wavelength (nm) and absorbance of $CoPcF_{16}$ -P4VP matrix in DMF solution after 30 days

Concentration CoPcF ₁₆ (mM)	$Q \lambda_{max} (nm)$	Absorbance
0.030	628	1.71
0.024	705	1.37
0.018	717	1.59
0.012	727	1.35
0.006	730	0.56



Figure 1. UV/Vis spectrum (a) $CoPcF_{16}$ in DMF solution; (b) $CoPcF_{16}$ -P4VP matrix in DMF solution at different concentration of $CoPcF_{16}$ after 30 days. Inset: Structure of $CoPcF_{16}$



Figure 2. UV/Vis spectra of CoPcF₁₆-P4VP matrix via time at 0.006 mM of CoPcF₁₆.

For the coordination of $CoPcF_{16}/P4VP$ matrix at low concentration, experiments were conducted for 7 days with 0.006 mM CoPcF_{16}. A broad Q band obtained at 636 nm in the beginning of the experiment.

Later, a small peak was observed at the lower intensity area at 673 nm. This new peak intensity increased via time till day 7 as exhibites in figure 2. The results suggest that dimeric structures formed in solution led to the aggregation and axial coordination between pyridine from P4VP chain and the Cobalt centre [12-13]. Nevin reported that the formation of dimeric species and aggregation resulting a shifted peak at 30-50 nm from the monomeric peak [14]. Ghani claimed that the unsubstituted CoPc is unstable and formed aggregates in solution with the value of maximum solubility in DMF solution is 0.174 mM [15]. However, the solubility of CoPc in polar or organic solvents increased with the substitution of electron-withdrawing group such as fluorine atom [16]. These observations indicated that CoPcF₁₆ is dispersed homogeneously in DMF solution before forming aggregates through time and at high concentration. There are three types of binding that probably occur in the solution (figure 3): (i) pyridine bind with the Co centre; (ii) the coordination formed between pyridine from the same polymer chain (intrachain); (iii) the coordination formed between different polymer chains (interchain).



Figure 3. Cartoon illustration of possible binding sites between $CoPcF_{16}$ and a P4VP chains in DMF solution.

The effect of axial coordination of $CoPcF_{16}/P4VP$ matrix was examined by interaction of $CoPcF_{16}$ and pyridine solution. Two conditions of experiment were selected which were an addition of 0.1% (v/v) pyridine solution to the 0.030 mM CoPcF₁₆ in DMF solution and 0.1% (v/v) 0.030 mM CoPcF₁₆ in DMF to pyridine solution. The UV/Vis spectrum was observed over 7 days and the results present in Figure 4. For 0.1% (v/v) pyridine in CoPcF₁₆, the Q band (650 nm) increase in intensity while the B band reduce via time. Whilst, the Q band obtained at 665 nm with a shoulder at 600 nm for 0.1% (v/v) CoPcF₁₆ in pure pyridine solution. After 300 minutes, both spectroscopic features have achieved their maximum intensity showing the coordination of pyridine with the Co complexes. The shoulders obtained suggest the dimeric species which was formed in the solution as demonstrated for other phthalocyanine complexes [7].

In contrast, $CoPcF_{16}/P4VP$ with the massive amount 4-vinylpyridine showed a changeable UV/Vis spectrum via time, while $CoPcF_{16}/pyridine$ spectrum is more stable. Obviously, the Q band shifted from 628 nm in DMF solution to 650 nm in diluted pyridine to 665 nm in pure pyridine. These outcomes are congruent with the model suggested above. At low pyridine concentration, one pyridine is bound to the metal centre, whereas two pyridine are coordinated to the metal centre at high pyridine concentration. Nevertheless, further work is needed to substantiate this idea because less aggregation is found in pure pyridine solution as compares to the P4VP containing solution. For P4VP solution, the broad Q bands (630 nm) is reduced with time due to the forming of new band at 670 nm. The following bands that

correspond to the increment of coordination of $CoPcF_{16}$ to the polymer chains. The coordination P4VP to $CoPcF_{16}$ by one or two unit pyridine remains unclear. The small variations observed in UV / Vis spectra of "pyridine coordinated compounds" is elucidated by solvent effects.



Figure 4. UV/Vis spectra of CoPcF₁₆-P4VP matrix *via* time (a) 0.3 mL pyridine (0.1% v/v) added into 3 mL CoPcF₁₆ 0.03 mM ; (b) 0.3 mL CoPcF₁₆ 0.03 mM (0.1% v/v) added into 3 mL pyridine.

4. Conclusion

The spectroscopic studies demonstrated that the solution that contains P4VP and CoPcF₁₆ change via time. The Q bands showed bathochromic shift indicating aggregation form in solution. The amount of coordinated CoPcF₁₆ increases with the amount of pyridine in solution especially P4VP. Based on the results, the coordination sites is suggested either one pyridine bind to the metal centre or two pyridine bind to the metal centre as interchain or intrachain conditions.

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International Conference of Chemistry (ICCHEM) 2018

IOP Conf. Series: Journal of Physics: Conf. Series 1156 (2019) 012010 doi:10.1088/1742-6596/1156/1/012010

Acknowledgment

The authors recognised the sponsorship given by Ministry of Higher Education (MOHE), Malaysia and Universiti Pendidikan Sultan Idris (UPSI).