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Optical properties of metal phthalocyanines

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Abstract In this study, optical properties of phthalocyanines of five metals, i.e., cobalt, nickel, iron, copper, and manganese, have been discussed in the energy (E) range of 1.5–4.1 eV. Utilizing the available data of refractive index (n) and extinction coefficient (k) of these materials in the literature, the related optical properties such as the real (ε_1), imaginary (ε_2) parts of the complex dielectric constant (ε), and reflectivity (R) are calculated. Interpretations for the energies corresponding to the peaks in ε_2 are explained in terms of the Penn gap (E_P). High-frequency dielectric constant (ε_∞) values corresponding to four models, i.e., the conventional Lorentz model, modified Lorentz model, relaxed Lorentz model, and the dual Lorentz model are used to determine E_P. It is found that the E_P values corresponding to the conventional and dual Lorentz models are in good agreement with the average of energy peaks in the R-E and the ε_2-E spectra. The oscillator energy (E_0) and the dispersion energy (E_d) of these materials have been determined utilizing the Wemple–DiDomenico model. The calculated values of (a) E_0 are generally in good agreement with the Penn gap E_P, the average of the energy peaks in the R-E and the ε_2-E spectra and (b) E_d are comparable to those in the literature for CoPc and NiPc.

Introduction

Phthalocyanines (Pcs) are macrocyclic compounds, and have attracted much attention due to their unique physical and chemical properties [1, 2]. In recent years, the applications of metal phthalocyanine (MPc) complexes have been expanded to include light emitting diodes [3], optical limiting devices [4, 5], liquid crystals [6], gas sensors [7–9], bio-sensors [10–12], photovoltaic cells [13, 14], photodynamic therapy [15–18], and in semiconductor materials [19, 20]. A mushroom-based cobalt phthalocyanine biosensor has been utilized for the determination of phenolic compounds [10]. A copper phthalocyanine chemoresistor has been used as a transducer in biosensing application [11]. It is important to note here that cobalt and nickel phthalocyanines may behave as carcinogens [21].

One of the most promising fields is the use of phthalocyanine derivatives as photosensitizers for photodynamic therapy (PDT), an emerging technology for treating a large variety of pathologies such as psoriasis, tumor, cancer, dysplastic, and infectious diseases [17]. While lipophilic phthalocyanine derivatives are reported to have a higher tumor affinity, associated with cutaneous phototoxicity [18], water soluble phthalocyanines are considered to be the best targets for a new generation of photosensitizers [16]. In a typical treatment of PDT, the patient receives an injection of the photosensitizer and waits for a short duration. This waiting period allows the photosensitizer to enrich in the tumor. Then, the tumor is illuminated by light with an appropriate wavelength. The excited photosensitizer causes a series of photodynamic reactions and destroys the tumor cell. Compared with traditional treatments such as surgery, iatrochemistry, and radiotherapy, the advantage of PDT is that it can destroy tumor selectively and does not harm the normal surrounding tissues seriously [1, 16]. During PDT, singlet oxygen is the predominant cytotoxic agent that is produced. This occurs when the photosensitizer undergoes electronic excitation from a ground singlet state to an excited singlet state; the excited singlet state is highly unstable, and rapidly

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undergoes intersystem crossing to a longer-living excited triplet state. One of the few chemical species present in the tissue is triplet state oxygen. When the photosensitizer and an oxygen molecule are in proximity, energy transfer takes place. It is this energy that is responsible for the spin inversion in molecular oxygen [16]. Therefore, in order to be used for PDT, a phthalocyanine must have a high yield of triplet state (and a concomitant high yield of singlet oxygen) and a long wavelength absorption in the red region of the visible spectrum [22]. MPc complexes have been proved as highly promising photosensitizers for PDT due to their intense absorption in the red region of the visible light. Complex structures of phthalocyanine with transition metals give short triplet lifetimes to these dyes. Closed shell and diamagnetic ions, such as Zn^{2+}, Al^{3+}, and Si^{4+}, provide phthalocyanine complexes with both high triplet yields and long lifetimes [15, 16]. Therefore, the optical properties of these MPcs are the key to their recent success within PDT.

Furthermore, in order to improve the overall performance of electronic, opto-electronic, gas- sensing, and biosensing devices, based on phthalocyanines, it is important to study the electronic and optical properties of MPcs to understand the complex nature of their excited states. Moreover, determination of optical properties such as refractive index (n), extinction coefficient (k), and dielectric constant ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) are interesting for many applications of MPcs [23]. In view of its numerous applications, the optical properties phthalocyanines of five metals, cobalt (Co), nickel (Ni), copper (Cu), iron (Fe), and manganese (Mn), have been discussed in this article. In particular, we discuss the spectral dependence of the optical constants; n, k, ε_1, ε_2, and reflectivity (R) of these MPcs. The real and imaginary parts of the optical dielectric constant, ε_1 and ε_2, are calculated using the phenomenological expressions:

$$\varepsilon_1 = n^2 - k^2 \quad (1)$$

$$\varepsilon_2 = 2nk \quad (2)$$

The reflectivity has been determined using the following expression:

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (3)$$

ε_1, ε_2, R, n, and k are functions of the photon energy, E.

Results and discussion

The analysis of the optical properties of metal phthalocyanines, i.e., CoPc, NiPc, CuPc, FePc, and MnPc, in this study, are based on the results of the energy dependence of the fundamental optical constants, n and k, in the literature [24–26]. The data of the optical properties, considered in this study, are those of thin films of CoPc, NiPc, CuPc, MnPc, and FePc deposited on glass substrates [24–26]. The thickness range of CoPc, NiPc, and FePc films is ~80–100 nm [24], CuPc is ~170 nm [25], and MnPc is ~204–630 nm [26].

Figure 1 shows the variations in n, k, ε_1, ε_2 and R with E for CoPc, NiPc, CuPc, MnPc, and FePc, in the spectral range of 1.5–4.1 eV (300–800 nm). It is evident from Fig. 1 that n, k, ε_1, ε_2 and R vary significantly with E. As can be seen in Fig. 1, ε_2-E and R-E spectra of CoPc, NiPc, and CuPc exhibit two sharp peaks and one broad peak; however, the corresponding spectra for FePc and MnPc exhibit one sharp peak and one broad peak. The energies corresponding to these peaks in the R-E and ε_2-E spectra of Fig. 1 are listed in Table 1. For the ε_2-E spectra, these energies, E_1, E_2, and E_3 in eV, respectively, are: (a) 1.81, 1.99, and 3.75 for CoPc (b) 1.82, 1.98, and 3.57 for NiPc, and (c) 1.80, 2.02, and 3.52 for CuPc. However, E_1 and E_3 for (d) FePc, respectively, are 1.94 and 3.54 eV, and for (e) MnPc, 1.70 and 3.45 eV. For R-E spectra, these energies, E_{R1}, E_{R2}, and E_{R3} in eV, respectively, are: (a) 1.76, 1.99, and 3.63 for CoPc, (b) 1.77, 1.98, and 3.54 for NiPc and (c) 1.73, 1.96, and 3.30 for CuPc. However, E_{R1} and E_{R3} for (d) FePc are 1.71 and 3.5 eV and for (e) MnPc, 1.71 and 2.81 eV. In addition to these peaks, FePc and MnPc also exhibit a small peak and shoulder in both the spectra and the corresponding energy values are listed in Table 1 in parentheses. In the ε_2-E spectra, FePc exhibits a small peak at 3.75 eV and a shoulder at 1.76 eV and MnPc exhibits a small peak at 2.31 eV and a shoulder at 1.97 eV. In R-E spectra, FePc exhibits a small peak at 3.74 eV and a shoulder at 1.9 eV and MnPc exhibits a shoulder at 1.97 eV.

Application of Penn model

The reflectivity spectra or the ε_2-E spectra of a given material are described by its band structure. Conceptually, the intensity maximum in ε_2 (or R) represents a maximum number in the optically induced electronic transitions in the material [27]. The energy corresponding to the peak in ε_2 (or R) should, therefore, correspond to band-to-band energy difference or a band gap. Since this is macroscopic gap [28], it should be related to the high-frequency dielectric constant ε_∞ ($\approx n^2$).

Several models have been proposed [28, 29] to interpret the frequency and wave vector dependence of the dielectric function. However, all these models have been proposed for elemental semiconductors. Extrapolations of the applicability of these models to amorphous semiconductors [30], narrow and wide-gap materials including alkali

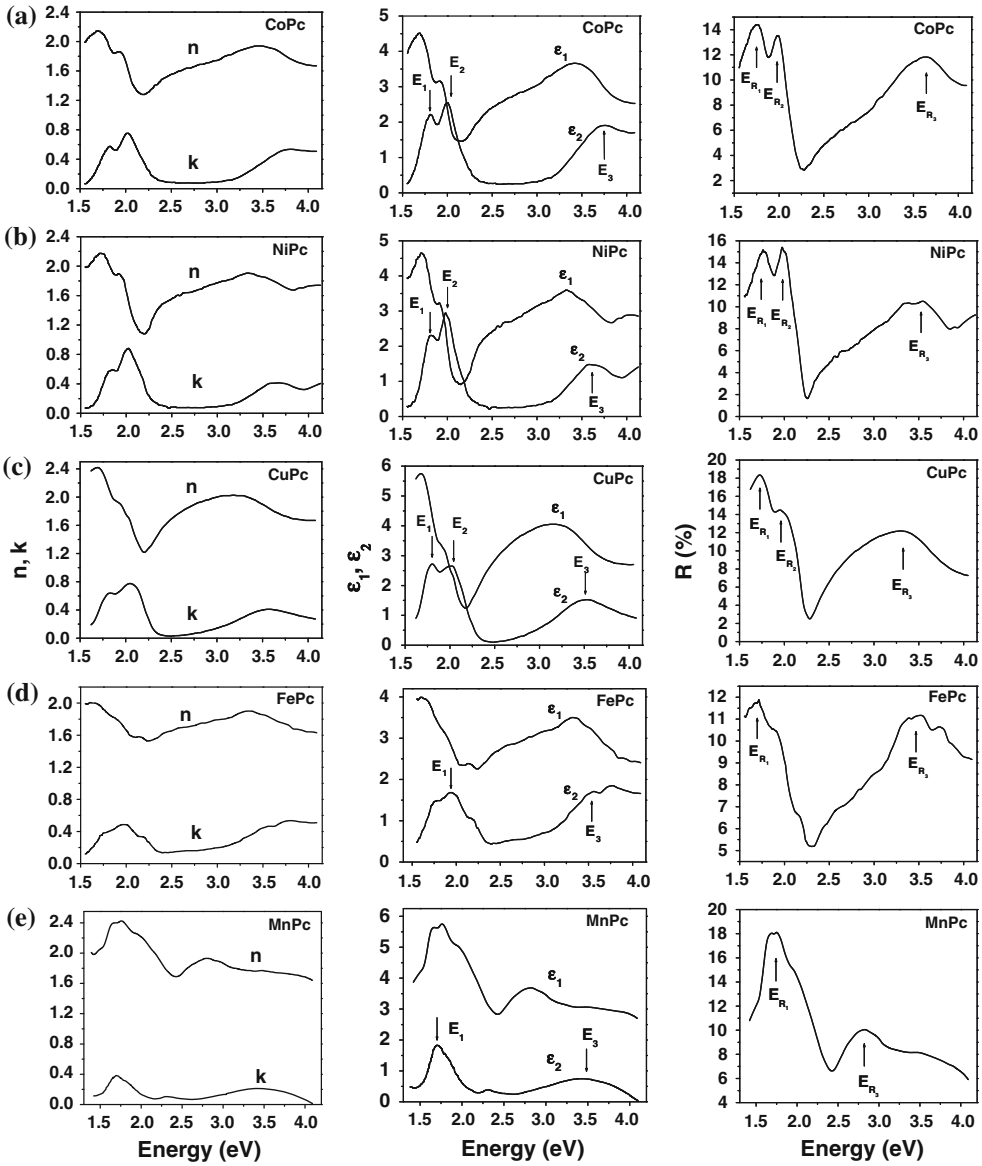

Fig. 1 Variation of n, k, ε_1, ε_2, and R as a function of photon energy for CoPc [24], CuPc [25], FePc [24], and MnPc [26]

Table 1 Reflectivity and ε_2 data of cobalt phthalocyanine, nickel phthalocyanine, iron phthalocyanine, copper phthalocyanine, and manganese phthalocyanine

MPc	E_1 (eV)	E_2 (eV)	E_3 (eV)	E_{R1} (eV)	E_{R2} (eV)	E_{R3} (eV)
CoPc	1.81	1.99	3.75	1.76	1.99	3.63
NiPc	1.82	1.98	3.57	1.77	1.98	3.54
CuPc	1.80	2.02	3.52	1.73	1.96	3.3
FePc	1.94		3.54	1.71		3.5
			(3.75)			(3.74)
			(1.76)			(1.9)
MnPc	1.70		3.45	1.71		2.81
			(2.31)			(1.97)
			(1.97)			

halides [31, 32] have been carried out with reasonable success. Here, we demonstrate the applicability of the model to these five metal phthalocyanines.

For a model semiconductor, ε_∞ is given by [28]:

$$\varepsilon_\infty = 1 + \left(\hbar\omega_p/E_p\right)^2\left[1 - \left(E_p/4E_F\right) + \frac{1}{3}\left(E_p/4E_F\right)^2\right] \quad (4)$$

or

$$1/E_p = 1/8E_F + \left[\left(\varepsilon_\infty - 1\right)/\left(\hbar\omega_p\right)^2 - \frac{1}{3}\left(1/8E_F\right)^2\right]^{1/2} \quad (5)$$

where, the valance electron plasmon energy $\hbar\omega_p$ is given by [33]:

$$\hbar\omega_p = 28.8(N_{eff}\rho/M)^{1/2} \quad (6)$$

In Eqs. 4 and 5, E_p is the Penn gap [28] or the macroscopic gap accounting for all the possible optically induced electronic transitions in the material, and E_F is the Fermi energy evaluated using the relation [32]:

$$E_F = 0.2947(\hbar\omega_p)^{4/3} \quad (7)$$

In Eq. 6, N_{eff} is the number of valence electrons per atom and is determined using the expression described elsewhere [34], M is the molecular weight, and ρ is the density of the metal phthalocyanine [2]. The values of ε_∞ for CoPc, NiPc, CuPc, and FePc are available in the literature [24]. In reference [24], the optical functions were determined by fitting the optical data obtained by spectroscopic ellipsometery (SE) measurements. The data were fitted with the conventional Lorentz model (CLM), modified Lorentz model (MLM), relaxed Lorentz model (RLM), and the dual Lorentz model (DLM). These model calculations have led to four values of ε_∞ [24]. These corresponding ε_∞ values have been used to calculate E_P. In CLM, the dielectric function ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) is given by [25, 35, 36]:

$$\varepsilon(\omega) = \varepsilon_\infty + \sum_j \frac{F_j}{\omega_j^2 - \omega^2 + i\Gamma_j\omega} \quad (8)$$

where, j is the total number of Lorentzian oscillators, and ω_j, F_j, and Γ_j are the peak frequency, strength, and broadening of the jth oscillator, respectively.

The dielectric function in MLM is given by the following Eq. [25]:

$$\varepsilon(\omega) = \varepsilon_\infty + \sum_j \frac{F_j}{\omega_j^2 - \omega^2 - i\Gamma'_j\omega} \quad (9)$$

where, j is the total number of Lorentzian oscillators, and ω_j, F_j, and Γ'_j are the peak frequency, strength, and broadening of the jth oscillator, respectively. Unlike CLM, where the width, Γ, is a constant, in MLM, Γ'_j, is a function of frequency given by [25],

$$\Gamma'_j(\omega) = \Gamma_j(\omega)\exp\left[-\alpha_j\left(\frac{|\hbar\omega| - \hbar\omega_j}{\Gamma_j}\right)\right] \quad (10)$$

where, α_j is the broadening factor of jth oscillator. If $\alpha_j = 0$, then the jth oscillator is a Lorentz oscillator. When $\alpha_j \sim 0.2$, then the jth oscillator is a Gaussian-like oscillator.The dielectric function in RLM is given by [35, 36],

$$\varepsilon(\omega) = \varepsilon_\infty + \sum_j \frac{F_j e^{i\beta_j}}{\omega_j^2 - \omega^2 - i\Gamma'_j\omega} \quad (11)$$

where, j is the total number of Lorentzian oscillators, and ω_j, F_j, Γ'_j, and β_j are the peak frequency, strength, broadening, and phase factor of the jth oscillator, respectively.The DLM is based on the classical Lorentz model [24]. The parameter Γ in the CLM represents the width of the oscillator. In DLM, each oscillator has two Γ values, one for the lower energy side of the peak and other one for the higher side. For each oscillator, the dielectric constant is assumed as below:

$$\varepsilon(\omega) = \varepsilon_\infty + \begin{cases} \dfrac{F}{\omega^2 - \omega_0^2 + i\Gamma_1\omega} & \omega < \omega_0 \\ \dfrac{F\Gamma_2}{\omega^2 - \omega_0^2 + i\Gamma_2\omega} & \omega \geq \omega_0 \end{cases} \quad (12)$$

where, ω_0 is the oscillator frequency, F is the oscillator strength, Γ_1 and Γ_2 are the two widths.

The results of these calculations are presented in Table 2. Table 2 also lists the values of band gap energy (E_g) for CoPc [37], NiPc [38] CuPc [38], FePc [39], and MnPc [26]. These values of E_g are determined from α^2 vs. $h\nu$ graph [26, 37–39]. The values of Penn gap, E_P, listed in Table 2, have been determined using Eq. 5 for the corresponding values of ε_∞. In Table 2, $\overline{E}_R$ represents the average of energies E_{R1} E_{R2}, and E_{R3} in the R-E spectra, and $\overline{E}$ represents the average of energies E_1, E_2, and E_3 in the ε_2-E spectra for CoPc, NiPc, and CuPc. However, for FePc and MnPc, $\overline{E}_R$ represents the average of energies E_{R1} and E_{R3} in R-E spectra, and $\overline{E}$ represents average of energies E_1 and E_3 in the ε_2-E spectra. The parenthesis value of $\overline{E}_R$ and $\overline{E}$ for FePc and MnPc represent the average of these two peaks, one small peak and a shoulder in the corresponding spectra.

As can be seen from Table 2, (a) for CoPc, the four E_P values are obtained for four ε_∞ values corresponding to four models (CLM, RLM, DLM, and MLM), the value of ε_∞ is 1.6 for CLM and DLM and the corresponding value of E_P (2.54 eV) for this value is very close to $\overline{E}$ and slightly differs with $\overline{E}_R$. However, for RLM ($\varepsilon_\infty = 1.43$) and MLM ($\varepsilon_\infty = 1.24$), the calculated values of E_P are higher than $\overline{E}$ and $\overline{E}_R$. The two reported values of ε_∞ for CoPc thin films are mentioned in parentheses, where $\varepsilon_\infty = 3.15$ corresponds to nanocrystalline CoPc film and $\varepsilon_\infty = 3.56$ corresponds to CoPc thin films [40]. The calculated values of E_P (in parentheses) corresponding to these ε_∞ values are 1.53 and 1.42 eV and noticeably differ with $\overline{E}$ and $\overline{E}_R$.

For (b) NiPc, the four E_P values are calculated for four models CLM ($\varepsilon_\infty = 1.55$), RLM ($\varepsilon_\infty = 1.49$), DLM ($\varepsilon_\infty = 1.73$), and MLM ($\varepsilon_\infty = 1.04$). The calculated value of E_P (2.41 eV) for DLM ($\varepsilon_\infty = 1.73$) is approximately equal to $\overline{E}_R$ and slightly differs with$\overline{E}$. However, for CLM and RLM, the obtained values of E_P are comparable to $\overline{E}$ and $\overline{E}_R$, for MLM ($\varepsilon_\infty = 1.24$), the calculated E_P (6.86 eV) is higher than $\overline{E}$ and $\overline{E}_R$. El-Nahass et. al. [41] have reported a value of $\varepsilon_\infty = 3.71$ for NiPc thin films. The

Table 2 Properties of metal phthalocyanines (CoPc, NiPc, CuPc, FePc, and MnPc)

MPc	Chemical formula	Mol. wt. (M)	ρ (g/cm^3)	E_g (eV)	N_{eff}	$\hbar\omega_p$	E_F (eV)	Model	ε_∞	E_P (eV)	$\overline{E}_R$ (eV)	$\overline{E}$ (eV)
CoPc	$C_{32}H_{16}N_8Co$	571	1.53	3.25 [37]	3.26	2.69	1.10	CLM	1.60	2.54	2.46	2.52
								RLM	1.43	2.88		
								DLM	1.60	2.54		
								MLM	1.24	3.53		
									(3.15) [40]	(1.53)		
									(3.56) [40]	(1.42)		
					(3.28)	(2.70)	(1.11)		1.60	(2.55)		
NiPc	$C_{32}H_{16}N_8Ni$	571	1.59	2.64 [38]	3.26	2.75	1.13	CLM	1.55	2.68	2.43	2.46
								RLM	1.49	2.80		
								DLM	1.73	2.41		
								MLM	1.04	6.86		
									(3.71) [41]	(1.42)		
					(3.28)	(2.75)	(1.14)		1.73	(2.42)		
CuPc	$C_{32}H_{16}N_8Cu$	576	1.61	2.71 [38]	3.26	2.75	1.14	CLM	1.39	3.05	2.33	2.45
					(3.24)	(2.74)	(1.13)		1.39	(3.04)		
FePc	$C_{32}H_{16}N_8Fe$	568	1.52	3.18 [39]	3.26	2.69	1.10	CLM	1.43	2.87	2.61	2.74
								RLM	1.42	2.90	(2.71)	(2.75)
								DLM	1.37	3.03		
								MLM	1.32	3.19		
					(3.28)	(2.70)	(1.11)	CLM	1.43	(2.88)		
MnPc	$C_{32}H_{16}N_8Mn$	567	1.52	3.25 [26]	3.26	2.69	1.10	2.65		1.71	2.26	2.58
					(3.28)	(2.70)	(1.11)			(1.71)	(2.16)	(2.36)
					(3.30)	(2.71)	(1.11)			(1.71)		
					(3.32)	(2.72)	(1.12)			(1.72)		
					(3.33)	(2.72)	(1.12)			(1.73)		
					(3.35)	(2.73)	(1.12)			(1.73)		

N_{eff} is the effective number of valence electrons per atom. $\hbar\omega_p$ is the valance electron plasmon energy. E_F is the Fermi energy. ε_∞ is the high-frequency dielectric constant. E_p is the Penn gap. $\overline{E}$ is the average of all the energies corresponding to the peaks in ε_2. E_g is the energy gap determined from α^2 vs. hν graph

corresponding E_P (in parentheses) is 1.42 eV which markedly differs with $\overline{E}$ and $\overline{E}_R$.

For (c) CuPc, the realistic value of ε_∞ is 1.39 for CLM; the other values of ε_∞ (RLM-1.00, DLM-1.02 and MLM-1.00) [24] are not acceptable to calculate Penn gap in accordance with Eq. 5. The calculated value of E_P is higher than both $\overline{E}$ and $\overline{E}_R$, however, E_P is more close to $\overline{E}$.

Also for (d) FePc, the four E_P values are obtained corresponding to four models, CLM ($\varepsilon_\infty = 1.43$), RLM ($\varepsilon_\infty = 1.42$), DLM ($\varepsilon_\infty = 1.37$), and MLM ($\varepsilon_\infty = 1.32$). E_P (2.87 eV), corresponding to CLM model is the closest value to $\overline{E}$ and $\overline{E}_R$. For RLM, DLM, and MLM, the calculated E_P is higher than $\overline{E}$ and $\overline{E}_R$.

For (d) MnPc, to the best of our knowledge, no previous data on ε_∞ has been reported in the literature. Therefore, ε_∞ ($\sim$2.65) is determined from the n versus k graph at high frequency at k ($\approx$0) [26]. The calculated value of E_P (1.71 eV) is lower than both $\overline{E}$ and $\overline{E}_R$ and differs considerably with $\overline{E}$.

It is important to note here that the closest E_P values 2.87 eV for FePc and 1.71 eV for MnPc, as discussed above are more close to their parenthesis values of $\overline{E}$ (average of energies corresponding to E_1, E_3, small peak, and shoulder) and $\overline{E}_R$ (average of energies corresponding to E_{R1}, E_{R3}, small peak, and shoulder), which shows the importance of Penn model in explaining the energy peaks in ε_2 -E (or R-E) spectra. The noticeable difference in E_P and $\overline{E}$ (or $\overline{E}_R$) may be attributed to the fact that ρ and ε_∞ mentioned in Table 2 for these MPcs do not pertain to the same MPcs on which the optical measurements were made. It is worthwhile to note here that such a procedure of comparing the calculated E_P with the average of the energies corresponding to the peak in ε_2 (or R) was proposed by Phillips [42].

From the above results, it can be concluded that for CoPc, NiPc, CuPc, and FePc, the determined E_P values corresponding to CLM and DLM are in good accord with E_P, $\overline{E}$ and $\overline{E}_R$.

It should be noted that, in these five MPcs; CoPc, NiPc, FePc, CuPc, and MnPc, the central metals are transition metals which have their valence electrons in more than one shell. Based on their outer configurations, Co ($4s^2$ $3d^7$), Ni ($4s^2 3d^8$), and Fe ($4s^2 3d^6$) may have 2 or 3 valence electrons. However, Cu ($3d^{10}4s^1$) may possess 1 or 2 valence electrons, and Mn ($4s^2$ $3d^5$) may have variation in valence electrons from 2 to 7. Therefore, in Table 2, we have also evaluated the Penn gap incorporating the variation in N_{eff} (in parentheses, in Table 2), for the calculation of E_P; ε_∞ is chosen such that E_P value is closest to $\overline{E}$(or$\overline{E}_R$) i.e., for CoPc, DLM, and CLM ($\varepsilon_\infty = 1.43$); for NiPc and DLM ($\varepsilon_\infty = 1.73$); for CuPc there is only one value, i.e., $\varepsilon_\infty = 1.39$; and for FePc and CLM ($\varepsilon_\infty = 1.43$). The values of N_{eff} and E_p in parentheses for CoPc, NiPc, FePc, and CuPc represent the situation when Co, Ni, and Fe have 3 valence electrons, and Cu has 1 valence electron. However, for MnPc, the values in parentheses correspond to variation in valence electron from 3 to 7. It is to be noted that the calculated values of E_P for these MPcs incorporating the variation in valence electron contribution is in good agreement with $\overline{E}$ (or $\overline{E}_R$). For CoPc, NiPc, CuPc, and FePc, the value of E_P in parentheses is approximately equal to the previous E_P value; however, for MnPc, the calculated E_P increases slightly for valence electron values of 6 and 7. These results suggest that the valence electrons present in the central metal (Co, Ni, Fe, Cu, and Mn) contribute to the effective number of electrons in corresponding MPcs, and hence, to their optical spectra of ε_2-E (or R-E). The successful extrapolation of the application of Penn-like models to theses metal phthalocyanines leads to interesting conclusions. An isotropic, nearly free electron model, such as the Penn model, seems to be valid for most materials, in explaining the energies corresponding to the peaks in the reflectivity spectra (or the (ε_2-E spectra) and correlating these energies to the band structure of the material.

At this stage, it would be worthwhile to look into n-λ(wavelength) variations. The well-known Wemple–DiDomenico model explains the n-λ behavior in the form [43]:

$$n^2(E) - 1 = \frac{E_d E_0}{E_0^2 - E^2} \tag{13}$$

where, E_d is the dispersion energy and is proportional to the volume density of valance electrons involved in the transitions at E_0, and E_0 is an average excitation energy or an interband transition energy (almost equal to Penn gap, Ref. [30]) coinciding with the energy corresponding to ε_2 max in the ε_2-E spectra. Thus, a plot of $1/(n^2 - 1)$ versus E^2 will be a straight line and yields values of E_d and E_0. Such variations of n vs. E (as in Eq. 13) is valid for photon energies less than the band gap [44]. It was found that the dispersion energy, E_d, which is related to the interband transition strength, obeys an extraordinarily simple empirical relation for over 100 widely different ionic and covalent nonmetallic crystals and liquids [43].

Figure 2 shows a plot of $1/(n^2 - 1)$ versus E^2 for the five metal phthalocyanines, CoPc, NiPc, CuPc, FePc, and MnPc. It is observed that the plots are linear over the energy ranging from 1.8 eV to approximately 2.8 eV. The values of E_0 and E_d are determined from the plot using the linear best fit parameters. These values are obtained from the intercepts and the slopes of the graphs of $1/(n^2 - 1)$ versus E^2 for CoPc, NiPc, FePc, CuPc, and MnPc. The values of E_d and E_0 are summarized in Table 3 for CoPc, NiPc, CuPc FePc, and MnPc. The respective values of E_d and E_0 for these phthalocyanines, in eV, are as follows: (a) CoPc: 3.29 and 2.19; (b) NiPc: 4.06 and 2.36; (c) CuPc:

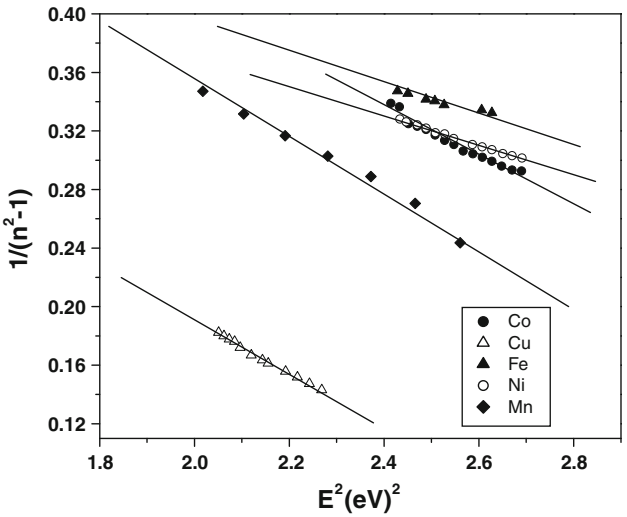

Fig. 2 Plot of $1/(n^2 - 1)$ versus E^2 for CoPc, NiPc, FePc, CuPc, and MnPc

Table 3 Wemple–DiDomenico parameters (E_d and E_0) of metal phthalocyanines (CoPc, NiPc, CuPc, FePc, and MnPc)

MPc	E_d (eV)	E_0 (eV)	Reported E_d (eV)	Reported E_0 (eV)
CoPc	3.29	2.19	3.28 [40]	1.52 [40]
			16.25 [40]	6.36 [40]
NiPc	4.06	2.36	3.50 [41]	8.06 [41]
CuPc	3.18	1.75	–	–
FePc	5.12	2.68	–	–
MnPc	2.77	1.98	–	–

3.18 and 1.75; (d) FePc: 5.12 and 2.68; and (e) MnPc: 2.77 and 1.98. El-Nahass et. al. [40, 41] have obtained the values of E_d and E_0 for CoPc and NiPc thin films, and their graphs of $1/(n^2 - 1)$ versus E^2 were linear in the range of 0.60 eV to approximately 1.16 eV. The reported values of E_d and E_0, in eV, for CoPc thin films are E_d: 3.28 and 16.25 and E_0: 1.52 and 6.36, where the higher energy values correspond to CoPc thin films, and the lower energy values correspond to nanocrystalline CoPc films [40]. As can be seen from Table 3, the determined and reported values of E_d and E_0 (corresponding to nanocrystalline CoPc film) are in good agreement. The determined E_0 (2.19 eV) value is comparable to $\overline{E}_R$ and $\overline{E}$.

The reported values of E_d and E_0 for NiPc thin films are 3.5 and 8.06 eV, respectively [41]. As can be seen in Table 3, the determined value of E_d, for NiPc, is comparable to the reported value. However, the determined E_0 value is lower than the reported value; this difference may be attributed to the difference in range of energies considered in the study and the fact that these represent thin films of metal Pcs on substrates. The determined E_0 (2.36 eV) value is very close to $\overline{E}_R$ and $\overline{E}$.

To the best of our knowledge, for CuPc, FePc, and MnPc, no previous data on E_d and E_0 have been reported in the literature. In this study, E_0 values for CuPc and MnPc are lower and noticeably differ with $\overline{E}_R$ and $\overline{E}$. However, for FePc, E_0 value is very close to $\overline{E}_R$ and $\overline{E}$.

Conclusions

Metal phthalocyanines have found applications in medicine and optoelectronics. The optical properties of five metal phthalocyanines, cobalt, nickel, iron, copper, and manganese, have been analyzed in this study. The available data of refractive index and extinction coefficient of these materials in the literature have been utilized to evaluate the relevant properties of these materials. Penn model leads to an explanation of the energies corresponding to the peaks in the ε_2-E spectra and the R-E spectra. High-frequency dielectric constant values corresponding to four models; conventional Lorentz model, modified Lorentz model, relaxed Lorentz model, and the dual Lorentz model were used to determine E_P. E_P values corresponding to CLM and DLM are in good agreement with the average of energy peaks in R-E and ε_2-E spectra. Oscillator energy, $E_{0,}$ and the dispersion energy, $E_{d,}$ have been determined using the Wemple–DiDomenico model. Interpretations for these energies have been sought in terms of the Penn model and have been compared with the results available in the literature.

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