

Strong Photophysical Diversity and the Role of Charge Transfer Excitons in Transition Metal Phthalocyanine β -Phases

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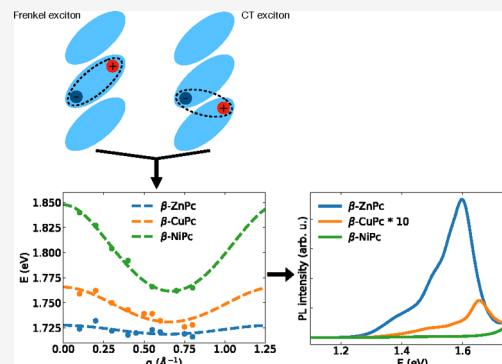
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ABSTRACT: The photophysics of the three transition metal phthalocyanines NiPc, CuPc and ZnPc in their β -phase has been studied using complementary experimental techniques: photoluminescence, optical absorption and electron-energy-loss spectroscopy. We demonstrate that the strongly different photoluminescence signal can be understood based on the different exciton dispersions, and that tiny differences in the structure and thus the intermolecular orbital overlap is able to model these differences. Our results clearly indicate a significant admixture of charge-transfer excitations to the lowest exciton state. They additionally demonstrate the need of a detailed microscopic understanding of organic semiconductors for their application potential.



INTRODUCTION

Expanding interest in organic semiconducting materials is driven by their potential application in a number of devices, among them light emitting or absorbing ones for display technology and photovoltaics.^{1–3} Clearly, the photophysical behavior of the materials determines that of the anticipated device. As a consequence, there is particular interest and need to fully understand the nature of electronic excitations in organic semiconductors connected with the aim to develop a deep understanding and a concomitant ability to model and predict the nature of the electronic excitations.

In this contribution we concentrate on a family of well-known organic semiconductors, the late transition metal phthalocyanines. These have also been subject of research for decades, but still there is a severe lack of understanding of fundamental phenomena. Until now, there is no consistent model, which explains the drastic changes of spectroscopic properties between NiPc, CuPc and ZnPc in their so-called β -structure, which is the thermodynamically stable phase. On the other hand, due to their high thermal and chemical stability they are promising candidates for optoelectronic devices, such as organic light emitting diodes^{4,5} or organic photovoltaic cells.^{6–9} Also medical applications due to their spectroscopic properties were discussed.^{10,11}

In the following, we significantly expand what is known from experiments on the optical absorption and on the luminescence behavior of the investigated phthalocyanines. We outline the drastic diversity in their photoluminescence (PL) behavior, from 'normal' PL for ZnPc to completely suppressed PL for NiPc, and we use optical absorption and in particular electron-energy-loss spectroscopy to comprehensively characterize the

electronic excitations. We demonstrate that the energetically lowest lying exciton exhibits very different properties. There is a quite large variation in the red shift of the optical absorption upon condensation into the solid state as well as a surprising, yet unknown difference in the exciton dispersion, no dispersion in β -ZnPc but visible negative dispersion in β -CuPc and in particular β -NiPc. We show that all these differences can be successfully modeled based upon a simple Frenkel-CT-exciton-model, and that the photophysics of these phthalocyanines substantially depends on the intermolecular orbital overlap. Our results demonstrate that tiny structural differences can result in tremendous variations of the exciton behavior and thus also the application potential of organic semiconductors.

METHODS

The ZnPc, CuPc and NiPc powders were purchased from Sigma-Aldrich. Physical vapor deposition was applied to prepare thin films with a thickness of about 120 nm on polished KBr single crystal and a silicon wafer kept at room temperature. The phthalocyanines were evaporated from ceramic crucibles at 635–675 K and at a base pressure of 10^{-8} mbar. Prior to thin film deposition, the silicon wafer was cleaned thoroughly by sonication in acetone. The evaporation rate was kept at 0.16 Å/s and was monitored with a quartz

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microbalance. This procedure resulted in thin films in the so-called α -phase which is typical for condensation of the molecules on a room temperature substrate^{12–14} and was verified by mid infrared spectroscopy (MIR), see Figure 1.

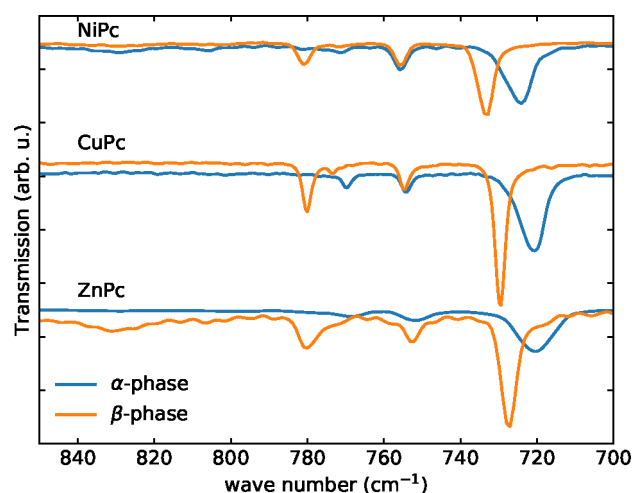


Figure 1. MIR transmission spectra of ZnPc, CuPc, and NiPc thin films in the α - and β -phases taken at room temperature.

MIR was measured at room temperature using a Bruker Vertex 80 V spectrometer. The structural phase can be identified through vibrational modes sensitive to the molecular arrangement in the structure,¹⁵ which can be observed in the range of 720 to 780 cm^{-1} .

A phase transition to the thermodynamically stable β -phase was induced by heating the samples for several hours at 575 K as has been reported previously.^{16–18} MIR transmission of the β -phase thin films shows a clear shift of the mode around 725 cm^{-1} as compared to the α -phase, and the appearance of a new mode at 780 cm^{-1} , see Figure 1.^{13,14}

Some metal phthalocyanine powder was dissolved in dimethylformamide (DMF) by sonication and filtered afterward to avoid agglomerates in the solution.

Visible absorption (VIS) spectra were measured at room temperature with a Bruker VERTEX 80 V spectrometer and at 77 K with the Hyperion microscope extension and a liquid nitrogen cooling stage. For the investigation of the photoluminescence (PL) behavior, steady-state emission spectra were induced with a Omicron PhoxX diode laser (638 nm) and detected with Avantes AvaSpec HS1024x122TEC high-sensitivity fiber-optic spectrometer with TE-cooled back thinned CCD detector, and an Andor Kymera Spectrograph with a Newton CCD camera. Variable temperature measurements were performed with fluorescence microscope of local design and Janis ST-500 microscopy cryostat (temperatures down to 4 K).

For EELS measurements, the thin films were transferred onto an electron microscopy grid. The KBr substrate was dissolved in distilled water. The floating thin film was then caught with the electron microscopy grid. The structural phase was verified by elastic electron scattering (diffraction) in the EEL spectrometer, which showed good agreement with calculated positions of the Bragg peaks.¹⁹ Taking the width of the first Bragg reflection feature allows us to estimate the long-range ordering. Crystallites in our thin films are not smaller than 8 to 10 nm. The detailed setup of the EEL spectrometer is described elsewhere.²⁰ For the experiment the

primary electron energy was 172 keV. During all measurements the samples were kept at 20 K to reduce radiation damage and thermal broadening. The EEL scattering rate is proportional to the so-called loss function, $I\left(-\frac{1}{\epsilon(q, \omega)}\right)$. Here q is the transferred momentum and $\epsilon(q, \omega)$ is the dielectric function of the sample. A detailed description can be found elsewhere.²¹

RESULTS AND DISCUSSION

We start the presentation of our results with a comparison of the optical absorption spectra of the β -phthalocyanine films in the visible range, as shown in Figure 2. This range

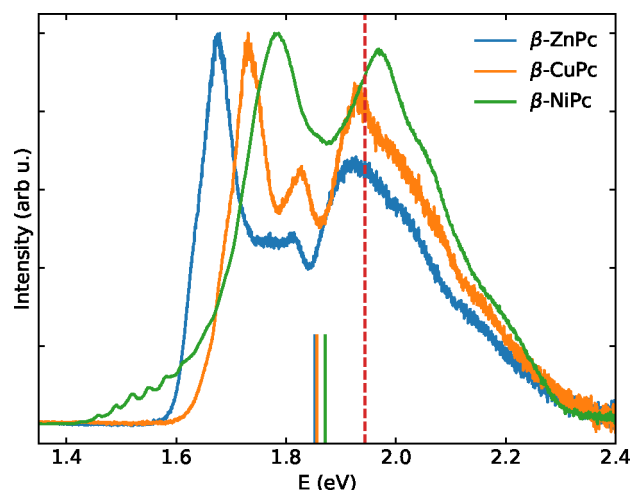


Figure 2. Visible absorption of thin films of ZnPc, CuPc, and NiPc β -phases at 77 K. Wiggles below the β -NiPc Q band are an experimental artifact due to the formation of ice on top of the film. Short vertical lines indicate the maxima of the ZnPc, CuPc, and NiPc molecules in DMF solution, respectively. Red vertical line denotes the PL excitation energy.

encompasses a strong absorption of phthalocyanines known as Q-band. The data in the figure agree very well with previously published results,^{13,22–24} and they additionally document the successful transformation of our films into the β -phase. The overall shape of the three spectra is similar, they are rather broad and consist of (at least) four components, visible as maxima or shoulders, respectively. A comparison to absorption data in the gas phase, in solution, or on surfaces for individual molecules, signals quite large solid-state effects on the absorption spectra.^{25–29} The absorption of individual molecules of all three investigated phthalocyanines consists of a single, narrow absorption line only, which is followed by small vibronic satellites, see Supporting Information. In Figure 2 the maximum of the solution absorption band of ZnPc, CuPc and NiPc is indicated by a vertical line, respectively. The excitation energies are almost the same, they differ by 18 meV only. The considerable changes on going to the solid phase has been discussed to be a consequence of a combination of effects.^{30–32} The lowest unoccupied molecular orbital of ZnPc, CuPc and NiPc molecules is 2-fold degenerate, this degeneracy is lifted due to a lower symmetry in the crystal or film and because the excited molecule is susceptible to a Jahn–Teller like distortion.^{22,33} Moreover, there are dipole–dipole interactions between the molecules in the solid phase with their neighbors. This often results in a visible energy shift of solid state spectra as compared to those from solution or the

gas phase. In addition, since the unit cell of β -phthalocyanines contains two molecules, a dipole–dipole interaction results in an energy splitting of the absorption signal, often termed as Davydov splitting.³⁴ However, both molecular distortions in the excited state as well as the dipole–dipole interaction are unable to explain the solid state absorption spectra as shown in Figure 2 quantitatively. This is especially true for the observed differences of the solid-state absorption spectra of the β -phthalocyanines.

Figure 2 demonstrates also the significant differences in the solid-state absorption data for the investigated β -phthalocyanines. While the data for ZnPc and CuPc are well structured with three clearly visible maxima, NiPc absorption only shows two broader features. Moreover, the absorption onset varies clearly, for ZnPc the absorption starts about 100 meV below that of NiPc, with CuPc being in-between. This difference in onset energy is much larger in comparison to the gas phase or solution data. These energies are summarized in Table 1. This

Table 1. Energetic Positions of the Lowest Q-Band Feature for Solution and β -Phase Thin Film Absorption^a

sample	solution	β -phase	Δ
ZnPc	1.853	1.670	0.183
CuPc	1.856	1.730	0.126
NiPc	1.871	1.773	0.098

^a Δ is the difference between the absorption onset in the solution and in the β -phase. All values are given in eV.

demonstrates that the interactions in the solid phase are quite different, despite the very close similarity in molecular and crystal structure, and the almost equivalent solution absorption data.

Additional intriguing insight into the photophysical behavior of the investigated β -phthalocyanines is provided by their PL behavior. In Figure 3 we present these data for β -ZnPc, β -CuPc and β -NiPc. These have been measured upon excitation into the upper part of the Q-absorption band with 638 nm light from a diode laser. Figure 3 demonstrates a dramatic and unexpected difference in the PL behavior. While β -ZnPc shows substantial

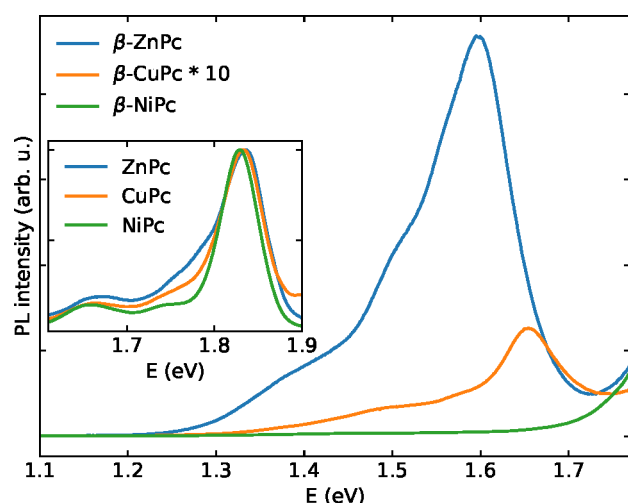


Figure 3. PL signal of β -ZnPc, β -CuPc, and β -NiPc at room temperature. Samples were excited with a 638 nm laser diode. Signal of β -CuPc was multiplied by 10. (Inset) Normalized PL of the ZnPc, CuPc, and NiPc molecules in DMF solution.

PL, the PL intensity of β -CuPc is considerably smaller, and β -NiPc does not show PL in the investigated energy range. This is in stark contrast to PL data from solution as shown in the inset of Figure 3, where the three Pc molecules exhibit very similar emission.

Our PL data for β -ZnPc and β -CuPc agree well in energy and spectral shape with what has been published previously.^{35,36} Also, it has been mentioned that for β -NiPc crystals no PL signal could be observed.³⁵

Thus, while ZnPc, CuPc and NiPc show virtually identical absorption and emission spectra in isolated molecular state, the optical absorption in the β -phase is visibly different, and the PL emission differs tremendously. An important difference between absorption and photoluminescence spectroscopy is that in the latter relaxation processes occur after excitation, which determine the final PL line shape and intensity. These processes comprise structural relaxations, nonradiative decay paths as well as a rearrangement of the electronic energies and occupation. Given the close similarity of the molecular orbitals and also the molecular optical absorption and PL of ZnPc, CuPc and NiPc, it is unlikely that intramolecular relaxation processes give rise to the dramatic differences in PL of the respective β -phases. As a consequence, solid-state interactions in the β -phases must be responsible for the PL variations.

Recently, we have shown that in β -CuPc,³⁷ the lowest singlet exciton is characterized by a negative exciton dispersion parallel to the molecular stacks in the crystal structure. In other words, the exciton has lower energies at finite momentum. Such an exciton dispersion is a direct consequence of the interactions of the molecules in the excited state. Though relatively small compared to some inorganic compounds (e.g., refs 38 and 39), exciton dispersions have been observed for organic molecular solids in the past and they have provided important insight into the character and behavior of these excitations.^{40–43} In particular, a negative exciton dispersion can have important consequences for the luminescence of the material. Provided that electronic excitations are able to relax to a lower energy state at finite momentum with the help of vibrations, their radiative decay is substantially suppressed due to momentum conservation, a situation which is found in indirect semiconductors such as silicon.

In Figure 4 we show the momentum dependence of the electronic excitation spectra of β -ZnPc, β -CuPc and β -NiPc films, measured by EELS. The figure shows a comparison of

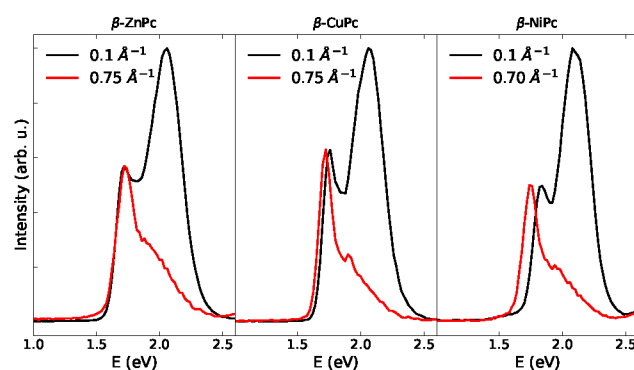


Figure 4. EEL spectra of ZnPc, CuPc, and NiPc β -phases. Black line corresponds to momentum transfer close to the center of the Brillouin zone (optical limit), whereas for red line represents the edge of the Brillouin zone. Curves were normalized to the first excitation feature for better visibility of the dispersion.

the spectra for very low momentum, i.e. the optical limit, and for a momentum close to the Brillouin zone boundary (along the molecular stacks in the crystal structure). The full data sets are shown in the [Supporting Information](#). In all cases, the spectra show a substantial change in spectral shape upon momentum change, a result which has been pointed out previously for CuPc already. More importantly, we observe a considerable difference in regard of the energy of the lowest excitation feature. This feature does virtually not change its energy upon momentum increase in β -ZnPc. In contrast, β -CuPc and in particular β -NiPc are characterized by a clearly visible negative energy shift for increasing momentum, a negative exciton dispersion. This negative dispersion is significantly larger for β -NiPc (see [Table 2](#)).

Table 2. Energy Shift of the First Excitation Feature Obtained from the EEL Spectra Shown in [Figure 4](#)

sample	ΔE (meV)
β -ZnPc	≤ 5
β -CuPc	33
β -NiPc	78

On the basis of these exciton dispersion data, the observed dramatic changes in the PL signal ([Figure 3](#)) can now be rationalized. In β -NiPc, after photoexcitation, there is relaxation to an exciton state with a finite momentum from which a direct radiative recombination is momentum forbidden. Thus, PL is strongly quenched. This relaxation is still possible but with less energy gain in β -CuPc, and it is not present in β -ZnPc, which in turn shows the brightest PL signal. In some sense this resembles the behavior of traditional indirect semiconductors (e.g., Si), but we emphasize that the electronic excitations in organic semiconductors are more complex and thus are the relaxation pathways.

Intriguingly, although the individual molecules are electronically almost equivalent and the crystal structures of the β -phases are very similar, the photophysical behavior of β -ZnPc, β -CuPc, and β -NiPc is significantly different. This difference must have its origin in the small variations of intermolecular interactions in the solid-state structures. Indeed, recent transport studies have revealed that the hole mobility also varies going from β -ZnPc to β -CuPc and β -NiPc.¹⁹ It has been shown that the hole mobility decreases by about a factor of 2, which is related to the slightly increasing molecular distance and hole hopping between the molecules along the molecular stacks in the crystal structure. The nature and dispersion of excitons can also be very dependent on such intermolecular interactions.

In recent years, it has been pointed out for some organic semiconductors that the molecular Frenkel excitons mix with so-called charge-transfer excited states (CT excitons), which can also lead to substantial changes of the absorption spectra as compared to single molecules.^{42–59} The most prominent example is pentacene, where it has been shown that the lowest singlet exciton has a CT admixture of almost 50% and that neither the energetic order nor the energy splitting of the two Davydov components can be rationalized without this significant CT contribution.^{48,51} A sizable admixture of CT excitons in the lowest excited state has also shown to be able to explain/model the exciton dispersion in oligoacenes.⁴⁸ Moreover, it has been shown that coherent electron and hole hopping are responsible for the exciton transfer integrals, the

exciton energy and wave function, and the observed dispersion. Analogously, we attribute the observed differences in exciton dispersion in the β -phthalocyanines to the small but decisive variations of intermolecular arrangement and concomitantly of electron and hole transfer integrals, which is supported by the different hole mobilities in β -ZnPc to β -CuPc and β -NiPc. We note that an interaction based on purely dipole–dipole interactions of molecular (Frenkel) excitons is unable to describe the spectra and the momentum dependence in the β -phthalocyanines (see below).

In order to achieve more quantitative insight into the exciton behavior and the intermolecular interactions, we adopt the approach published by Hestand and Spano in their pioneering work.^{46,55} In this way we follow the notion that the exciton behavior and delocalization are predominantly determined by the intermolecular hopping parameters of the holes and electrons. Moreover, these hopping parameters also govern the admixture of local Frenkel excitons and charge transfer excitons. This is schematically depicted in [Figure 5](#). We aim

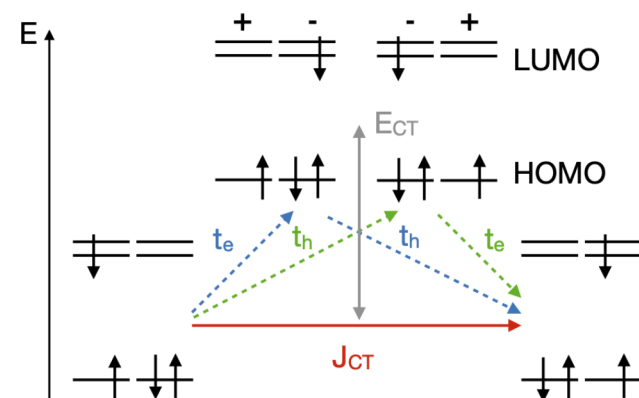


Figure 5. Schematic coupling of Frenkel and CT (–,+) excitons in MPcs in the style of Hestand and Spano.⁵⁵ Green and blue arrows denote the two pathways of charge carrier hopping.

at a description of the lowest exciton as a mixed Frenkel–CT exciton only. We are well aware of the fact that this simplification cannot describe the full photophysics of phthalocyanines (for an overview of the manifold processes that contribute to the excitation behavior, see ref 60). For instance, the lowest excited state of the individual molecules is 2-fold degenerate (the LUMO is 2-fold degenerate). Although this degeneracy is lifted in the solid state (see above), there are two close-lying molecular excitations (Frenkel-type excitons) which are not considered further. Also, there are two types of charge transfer excitons, and both intermix with the two Frenkel-type excitations. In our description, we include Coulomb coupling to the nearest neighbors in the one-dimensional stacks of the phthalocyanine molecules in the β -phases.

The simplifications notwithstanding, the simplest one-dimensional model considering a Frenkel and a charge transfer exciton together with their coupling and delocalization via electron and hole hopping will provide us with further insight into the behavior of the energetically lowest exciton in the phthalocyanines. The momentum dependence of the mixed Frenkel–CT exciton energy can be derived as⁵⁵

$$E(q) = \frac{E_{CT} + E_F(q)}{2} - \sqrt{\left(\frac{E_{CT} - E_F(q)}{2}\right)^2 + 2(t_e^2 + t_h^2 + t_e t_h \cos(q))} \quad (1)$$

with

$$E_F(q) = E_F(0) + 2J_{Coul} \cos(q) \quad (2)$$

E_F and E_{CT} are the energies of the molecular Frenkel and CT exciton, J_{Coul} describes the Coulomb coupling of the Frenkel excitons, t_e and t_h are the electron and hole hopping integrals, and q is the momentum.

The intermolecular dipole–dipole coupling J_{Coul} was calculated using the point dipole approximation $J_{Coul} \approx \frac{\mu^2(1 - 3 \cos^2(\theta))}{4\pi\epsilon R}$. We used the structural data of β -phase MPcs,¹⁹ and we adopt a dipole moment μ of 1.43 D^{22,27,61,62} and a dielectric constant ϵ of 4.0⁶³ for all three phthalocyanines. For $E_F(0)$ we used the absorption energy of the individual molecules in solution, see Table 1. The resulting Coulomb coupling constants indicate that in the absence of charge transfer the lowest Frenkel exciton would form a J-like aggregate, as has been obtained by DFT calculations on a ZnPc dimer structure previously.⁶⁴ However, the size of J_{Coul} is unable to explain the observed differences between the investigated phthalocyanines, and the negative exciton dispersion in CuPc and NiPc is in contradiction to a J-aggregate formation. Thus, the main intermolecular coupling must be provided by hole and electron hopping and the admixture of CT excitons, as outlined in the equation above and in good agreement with the results from recent calculations of the excitation behavior of ZnPc aggregates.⁶⁰

In consideration of the equation above and the virtually absent dispersion of the lowest exciton in β -ZnPc, it becomes clear that one of the hopping parameters must be very small (almost zero) in β -ZnPc. As the largest hole mobility has been reported for this material compared to β -CuPc and β -NiPc,¹⁹ we infer that the electron hopping in β -ZnPc is close to zero. In addition, with the largest hole hopping we can describe the largest red shift compared to the gas phase in the absorption spectra of β -ZnPc. The more strongly negative dispersion for the other two phthalocyanines can only be rationalized with electron and hole hopping of different sign. Taking these facts into account, we can quantitatively describe the momentum-dependent energy position in all three cases using the parameters as shown in Table 3. This is presented in Figure 6.

The values given in the table indicate that the energy of the charge transfer exciton E_{CT} is virtually the same for all three investigated phthalocyanines. This is not very surprising in view of the very similar crystal structures, molecular arrange-

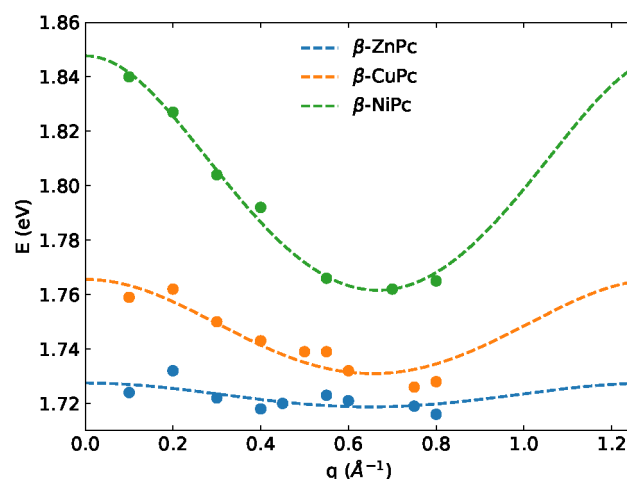


Figure 6. Simulated exciton dispersion and EELS data (dots) of the lowest exciton obtained using eq 1 and the parameters in Table 3.

ments, and distances: the electrostatic binding energy of the CT exciton can be estimated by $e^2/(\epsilon_0\epsilon_{PC}R)$, with R being the distance of the involved molecules and ϵ_{PC} representing the electrostatic screening of this interaction in the Pc crystal.

In contrast, the obtained values for electron and hole hopping vary significantly for the phthalocyanines. Hole hopping t_h shows a decreasing trend going from β -ZnPc to β -CuPc and β -NiPc. This is in good agreement with previous transport studies, which reported that the hole mobility in β -ZnPc is the largest of the three phthalocyanines and qualitatively decreases in the same manner.¹⁹ Interestingly, the opposite trend is observed for the electron hopping t_e . Consequently, our data indicate that despite the very similar crystal structures there are tiny differences that substantially change the intermolecular overlap of the HOMO and LUMO of adjacent molecules in the three investigated phthalocyanines. Moreover, these variations result in a completely different exciton dispersion and luminescence behavior. Finally, according to Hestand and Spano,⁵⁵ the behavior of β -NiPc, a considerable negative exciton dispersion, and a suppressed PL signal arise from a charge transfer H-aggregate formation. The opposite sign of t_e and t_h also for CuPc and ZnPc points in the same direction but is much less pronounced.

CONCLUSION

We demonstrated a largely diverse photophysical behavior of the late transition metal phthalocyanines NiPc, CuPc, and ZnPc in the thermodynamically stable β -phases. Despite the close similarities in crystal structure, the luminescence behavior ranges from bright emission (β -ZnPc) to completely absent emission (β -NiPc). In addition, further clear differences can be seen in the optical absorption data and in particular the exciton dispersion. The suppressed luminescence in β -NiPc is due to a significant negative exciton dispersion, which provides a relaxation path for photoexcitations into a state where luminescence is momentum forbidden. We can describe the behavior based upon a simple Frenkel–CT model,⁵⁵ including hole and electron transfer integrals. This model indicates that these transfer integrals substantially vary between the three phthalocyanines. Moreover, we predict increasing electron hopping going from β -ZnPc to β -NiPc, opposite to what has been reported for hole transport. Our analysis demonstrates that the photophysical behavior of molecular organic semi-

Table 3. Resulting Parameters by Fitting eq 1 to the EELS Data^a

sample	E_{CT}	J_{Coul}	t_e	t_h	t_h from ref 19
β -ZnPc	2.004	−3.6	−7.1	135.0	44.8
β -CuPc	1.997	−3.3	−17.0	115.4	35.8
β -NiPc	2.101	−3.0	−46.6	93.4	22.3

^a J_{Coul} was calculated using the point dipole approximation. E_{CT} is given in eV; all other parameters are given in meV.

conductors can be considerably dependent on relatively small structural variations which may in some cases provide a successful route to tune the optical properties.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.1c02654>.

Visible absorption of the metal phthalocyanines in dimethylformamide solution; electron energy loss spectra of metal phthalocyanine β -phases (ZIP)

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Notes

The authors declare no competing financial interest.

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