

New charge-transfer states in blends of ZnPC with F8ZnPC

Cite as: AIP Advances 11, 025230 (2021); <https://doi.org/10.1063/5.0037958>

Submitted: 17 November 2020 . Accepted: 14 January 2021 . Published Online: 12 February 2021

 Lukas Graf,  Katrin Ortstein,  Louis P. Doctor, Marco Naumann,  Jan Beyer, Johannes Heitmann, Karl Leo, and Martin Knupfer



View Online



Export Citation



CrossMark

ARTICLES YOU MAY BE INTERESTED IN

[Coherent optical interaction between plasmonic nanoparticles and small organic dye molecules in microcavities](#)

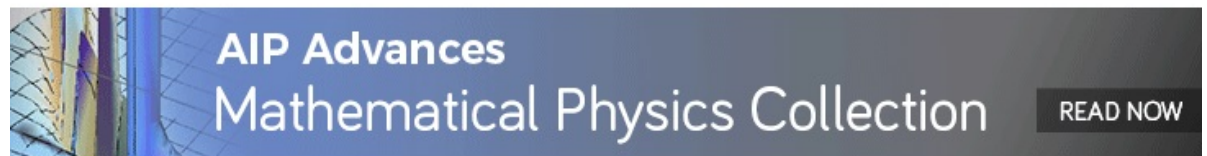
Applied Physics Letters **118**, 013301 (2021); <https://doi.org/10.1063/5.0027321>

[Modeling photocurrent action spectra of photovoltaic devices based on organic thin films](#)

Journal of Applied Physics **86**, 487 (1999); <https://doi.org/10.1063/1.370757>

[Tuning the ambipolar behaviour of organic field effect transistors via band engineering](#)

AIP Advances **9**, 035202 (2019); <https://doi.org/10.1063/1.5080505>



New charge-transfer states in blends of ZnPC with F8ZnPC

Cite as: AIP Advances 11, 025230 (2021); doi: 10.1063/5.0037958

Submitted: 17 November 2020 • Accepted: 14 January 2021 •

Published Online: 12 February 2021



View Online



Export Citation



CrossMark

Lukas Graf,^{1,a)}  Katrin Ortstein,² Louis P. Doctor,¹  Marco Naumann,¹ Jan Beyer,³  Johannes Heitmann,³ Karl Leo,² and Martin Knupfer¹

AFFILIATIONS

¹Leibniz Institute for Solid State and Materials Research Dresden, Helmholtzstraße 20, D-01069 Dresden, Germany

²Dresden Integrated Center for Applied Physics and Photonic Materials (IAPP) and Institute for Applied Physics, Technische Universität Dresden, D-01062 Dresden, Germany

³TU Bergakademie Freiberg, Institute of Applied Physics, Leipziger Str. 23, D-09596 Freiberg, Germany

^{a)} Author to whom correspondence should be addressed: l.graf@ifw-dresden.de

ABSTRACT

With the aim of pushing the knowledge and understanding on mixed films of organic semiconductors forward, blends of ZnPC and F8ZnPC in different ratios are manufactured. The films have a polycrystalline structure, as indicated by electron diffraction profiles and infrared-spectroscopy. Photoluminescence data show completely different spectra for the blends, compared to the pure materials, which can be ascribed to the suppressing of excimer formation and the appearance of a new charge-transfer excitation between the two different molecules in the blends. This new excitation can also be seen in optical absorption. Momentum dependent measurements of the electronic excitations by electron energy-loss spectroscopy confirm the localized character of the new charge-transfer excitation in the blends. Our experimental data help understand the important issue of donor/acceptor coupling in organic semiconductors.

© 2021 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). <https://doi.org/10.1063/5.0037958>

I. INTRODUCTION

Semiconductor devices have become an integral part of the daily life, and for some years now, organic semiconductor devices have become increasingly present, e.g., as organic light emitting diodes (OLEDs) for displays in smartphones or TVs. To realize efficient devices, it is essential to create perfectly adapted energy structures, regardless of the material. In inorganic materials, this is achieved by mixing compound semiconductors such as GaAs with, e.g., AlAs. However, this approach did not seem to be possible in organic semiconductors since these exhibit localized electronic states instead of delocalized Bloch states. While first indications showed tunability in organic solar cells in 2013,¹ Schwarze *et al.* showed in 2016² that a controlled shift of the ionization energy (IE) can also be achieved in organic semiconductors by mixing molecules with a halogenated derivative. This effect is based on interactions of excess charge carriers with the quadrupole field in the thin film. The model system for these studies was zinc phthalocyanine (ZnPc) and its fluorinated derivatives.³ These materials are known, *inter alia*, as

absorber and donor materials in organic solar cells^{4–8} but are also employed in OLEDs.^{9,10} The fluorinated derivatives are particularly characterized by the fact that the fluorination shifts the energy levels down with respect to the vacuum level, while the strength of the shift depends on the number of fluorine atoms.^{11,12}

Mixtures of other phthalocyanines with their fluorinated derivatives have already been investigated; however, the focus was on the analysis of the film structure, the optical properties, and the mobility of the charge carriers.^{13–15} Based on Schwarze *et al.*, the influence of quadrupole moments on different properties of thin films and devices has been increasingly investigated in recent years and ZnPc:F8ZnPc mixtures came into the field of attention for application in organic field effect transistors (OFETs),^{16,17} also in combination with doping.^{18,19}

The aim of this paper is to provide insight into the behavior of the electronic excitations in such blended layers and thus to achieve a full picture of the effects that can occur. For this purpose, we first apply infrared (IR) measurements to determine the growth phase and the mixing ratio in the mixed layers. Subsequently,

we discuss photoluminescence (PL) and UV-vis spectra and use electron energy-loss spectroscopy (EELS) to check the momentum dependence of the absorption features.

II. RESULTS AND DISCUSSION

A. IR-spectra

Thin mixed films (blends) with the molar ratios ZnPC:F8ZnPC 1:0, 3:1, 1:1, 1:3, and 0:1 were prepared via vapor deposition. In Fig. 1, we present the IR-absorption data. The top curve shows the spectrum of pure ZnPC, followed by those for the various blends and pure F8ZnPC as indicated. In addition, the vertical lines denote wave numbers that represent absorption by ZnPC (red lines), F8ZnPC (purple lines), or both (gray lines).

The top spectrum of ZnPC is in very good agreement with those reported in the literature for α -ZnPC.^{20,21} In combination with the electron diffraction data (see the [supplementary material](#)), this proves that our ZnPC films did predominantly grow in the so-called α -phase. For F8ZnPC, the electron diffraction data agree well with the literature (see the [supplementary material](#)). The relative spectral weight of the IR-absorption peaks that stem from either ZnPC or F8ZnPC only is expected to represent the mixing ratio in our blends. Indeed, one can see that the ZnPC related peaks decrease upon increasing the amount of F8ZnPC in the blend and vice versa. Moreover, the respective peak ratios confirm the changes in the composition of our blends (for further analysis, see the [supplementary material](#)). Finally, neither the IR data nor the electron diffraction showed a polarization or direction dependence, which demonstrates the polycrystalline structure of all films.

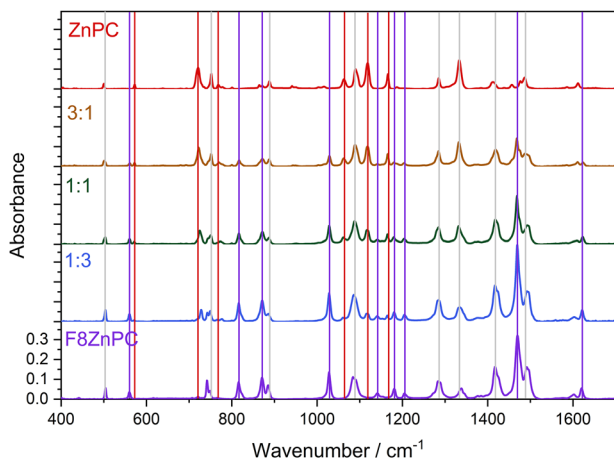


FIG. 1. IR-spectra for different mixing ratios with pure ZnPC at the top and pure F8ZnPC at the bottom. Red lines denote typical peaks of ZnPC, purple lines denote typical peaks of F8ZnPC, and gray lines denote peaks that are present in the spectra of both materials. The spectra of the pure materials confirm the growth in the α -phase, and a clear transition from one material to the other is visible in the peak intensities of the blends. The IR modes as depicted in this figure can be roughly classified into four subgroups, which are further discussed in the [supplementary material](#).

B. UV-vis spectra

In Fig. 2(a), optical absorption data at 77 K of the blends as well as the pure materials are shown. Again, the data for the pure materials agree well with previously published measurements.^{22–24} Often, the absorption spectra of phthalocyanines in the energy range shown in Fig. 2(a) are referred to as Q-band. This Q-band absorption originates from a highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) transition. It is characterized by a substructure that is caused by a combination of symmetry reduction, i.e., lifting of the LUMO degeneracy, Davydov-splitting, and vibrational coupling.^{24–26}

Given the similarity of the data for the two pure materials, it is not surprising that the data for the blends also look relatively similar. However, zooming into the energy region below the absorption onset of the pure materials reveals an additional small absorption feature, as demonstrated in Fig. 2(b). Clearly, absorption at energies 1.5 eV–1.6 eV occurs in the blends. We assign this first absorption peak to a charge-transfer (CT) excited state of a pair of ZnPC and F8ZnPC, as is schematically depicted in Fig. 3. Such pairs are present in all blends, independent of the mixing ratio. Since fluorination of ZnPC significantly shifts the molecular energy levels as, for instance, observed in photoelectron spectroscopy studies,^{2,27,28} a new charge-transfer (CT) excited state is possible in the blends at energies below the absorption onset of the two pure materials, with the hole residing in the highest occupied molecular orbital (HOMO) of the ZnPC and the associated electron in the lowest unoccupied molecular orbital (LUMO) of the adjacent F8ZnPC. The slight differences of the observed CT peak positions (1.55 eV, 1.57 eV, and 1.49 eV for the mixtures 3:1, 1:1, and 1:3, respectively) most likely result from the different next-nearest neighbor combinations that are possible in the blends, i.e., with increasing admixture of F8ZnPC to the blend polarization screening of the CT excitation might change as well and give rise to small energy differences (up to 80 meV).

C. PL spectra

A CT excited state as concluded above is also visible in the photoluminescence (PL) spectra of the blends. In Fig. 4, we present the PL data for pure ZnPC and F8ZnPC as well as for the three blends taken at 13 K. Figure 4 demonstrates that the PL spectra of the three blends differ substantially from those of the pure materials. ZnPC shows main emission around 1.2 eV and 1.3 eV followed by a small feature at around 1.45 eV, while the data for F8ZnPC are characterized by two emission features at about 1.25 eV and 1.4 eV. These results are in good agreement with previous reports.^{20,22,23} PL at these energies well below the optical absorption onset (at about 1.6 eV, see above) has been interpreted to be a consequence of excimer formation in pure ZnPC and F8ZnPC,²² a process that is common to a number of organic semiconducting materials and that results in a relatively strong red shift of the luminescence signal compared to optical absorption.²⁹

In contrast, the ZnPC:F8ZnPC blends are characterized by two prominent emission maxima at about 1.5 eV and 1.8 eV. These maxima are relatively broad, and the peak positions are rather independent of the mixing ratio in the blends, while the relative emission intensity shows slight variations with the mixing ratio. Considering the clear difference in PL between the pure materials and the blends, it is evident that emission occurs from different excited states. In

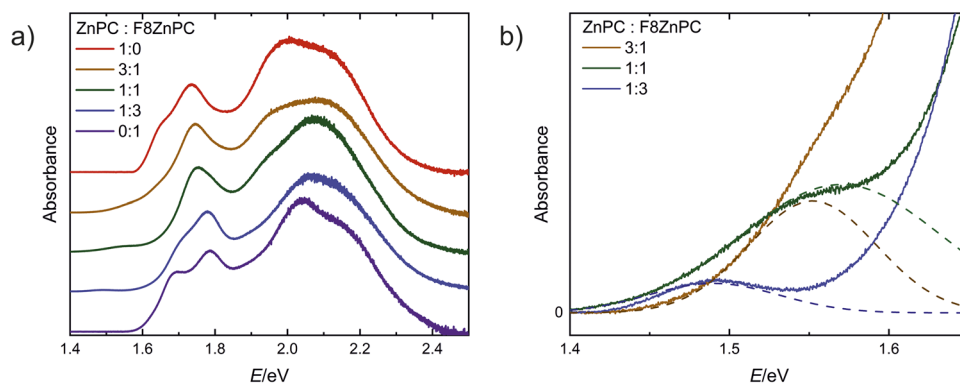


FIG. 2. Optical absorption data for ZnPC, F8ZnPC, and the blends [Fig. 2(a)]. Figure 2(b) focuses on the energy range close to the absorption onset. The new CT-related peaks are denoted by dashed lines.

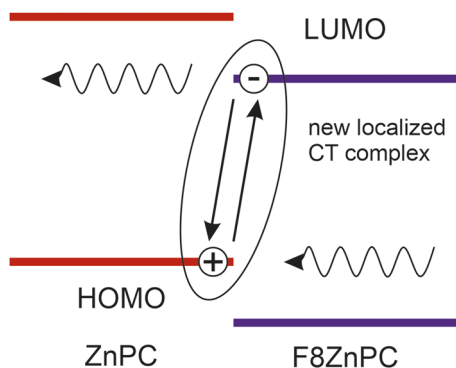


FIG. 3. Schematic energy level diagram for mixed pairs in the ZnPC:F8ZnPC blends. The new CT excitation is outlined.

the mixed films, excimer formation is likely to be suppressed since it requires a particular arrangement of two molecules with the possibility to form an excited dimer after excitation. In the blends, the neighboring molecules can change in type and position, and both will result in a suppression of excimer formation and the associated PL signal.

The PL of the blends (Fig. 4) still starts below the optical absorption onset of the two materials involved (see above). Following the above discussion, we attribute the first emission peak to arise from CT excitations in ZnPC–F8ZnPC pairs; see Fig. 3. Since the energy of this CT state is lower than the absorption onset of the two individual materials, PL can appear at lower energies as compared to the absorption of the pure materials. We note that the blends of ZnPC and F8ZnPC do not form a charge-transfer salt, i.e., there is no charge transfer in the electronic ground state of the blends. This is documented by previous photoemission data,² which could be modeled very well on the basis of a superposition of ZnPC and F8ZnPC molecular spectra.²

The second emission feature of the blends at about 1.8 eV cannot arise from the CT state. We interpret this feature as the emission from ZnPC or F8ZnPC molecules, which appears in the blends due to the different nearest neighbors and disorder in

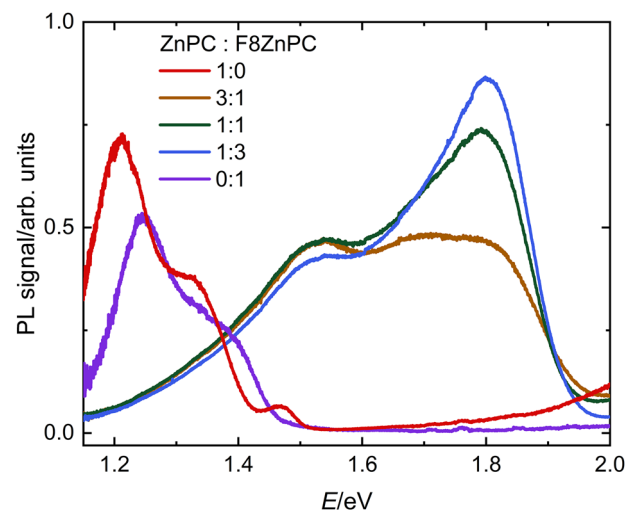


FIG. 4. PL spectra of ZnPC, F8ZnPC, and the blends. The spectra of the blends are shifted drastically to higher energies compared to the spectra of the intrinsic layers caused by a suppression of the excimer formation. The emission peak at about 1.5 eV can be attributed to the new CT exciton, and the second peak at 1.8 eV arises from the single molecule emission of the molecules.

the blends as compared to the pure films. These effects suppress emission from excimer states as observed for the pure films. The energy of 1.8 eV agrees well with emission from single ZnPC molecules in gas phase and solution, which is in good agreement with this interpretation.^{30–32}

In addition, we assign the very broad emission features to a combination of two effects: the disorder induced energy differences of the molecular orbitals, as the molecular arrangement in the mixed films is statistically disordered, and vibrational broadening. A comprehensive microscopic description of the entire emission spectra would require a detailed theoretical analysis, which is beyond the scope of this paper. We emphasize that the energy of the lowest emission peak (1.5 eV) in the blends corresponds very well with the excitation energy as observed in the optical absorption data,

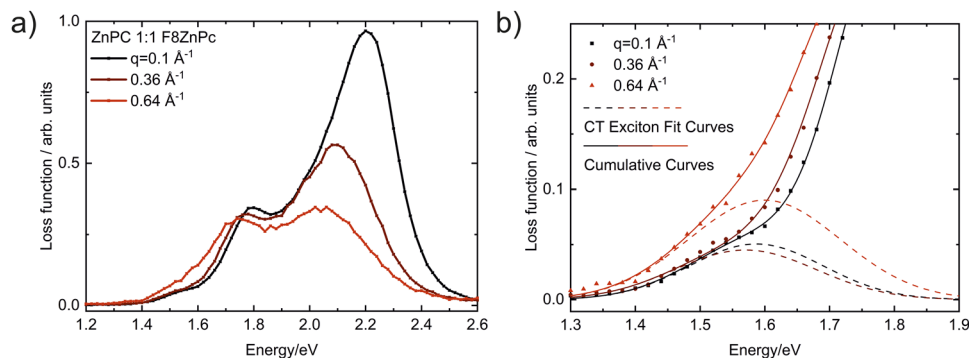


FIG. 5. (a) EELS spectra of the 1:1 blend at different momentum values. Figure (b) shows the fitted spectra with a focus on the charge-transfer exciton. The localized character of the CT exciton is clearly visible as it disperses less than 20 meV.

which supports our assignment to a new CT related excitation in the blends.

Comparing the data from luminescence and absorption measurements shows that the PL signal of the charge-transfer states provides a significant contribution to the corresponding spectra, while the direct excitation of this charge-transfer state appears rather weak in the absorption data. This is most likely related to the relaxation mechanisms that occur before the luminescence decays, which result in a high occupation of the CT state. The direct excitation in the absorption process is weak due to the small matrix element for transition to a neighboring molecule. A comparison of the optical absorption data and those from luminescence measurements reveals a negligible Stokes shift. This corresponds well to the observed very small Stokes shift of about 20 meV only, which has been observed for ZnPC in solution³² and the absence of a Stokes shift for ZnPC in cryo-matrices.³³ Moreover, looking at gas phase absorption data of phthalocyanines,³⁴ it is evident that vibrational satellites are very weak as compared to other organic semiconductor molecules such as the oligoacenes. This demonstrates a comparatively weak molecular relaxation in the excited state and also explains a small Stokes shift.

D. EELS spectra

Finally, our interpretation of the lowest absorption features in the ZnPC:F8ZnPc blends implies that this excitation is localized to a pair of molecules and thus should not show visible dispersion, i.e., visible energy-momentum dependence. Vice versa, dispersion of non-localized excited states in organic semiconductors can occur and has been observed at some materials in the past.^{35–37} The method of choice for a measurement of such dispersion is electron energy-loss spectroscopy (EELS). We have performed EELS measurements of the ZnPC:F8ZnPc blend with 1:1 composition, as shown in Fig. 5.

The black curve for 0.1 \AA^{-1} momentum transfer is the spectrum in the optical limit. It can be compared to the optical absorption spectra. Note that the spectra from absorption and EELS are not identical since a different response function is probed. Nevertheless, the two spectra agree in the appearance of two main excitation features. The fine structure as seen in the optical data is absent in the EELS spectra due to much worse energy resolution. Importantly,

the additional new CT feature as found in the blends is also seen in the EELS data. Its onset is at about 1.4 eV. Going to higher momentum transfer, the second main maximum shows a clear downshift in energy. The feature at around 1.8 eV also shows a downshift. This is in good agreement with previous data on pure phthalocyanines and can be interpreted as a negative dispersion of respective excitations.³⁷ The spectral onset, however, does not show a momentum dependence, signaling the localized character of the corresponding excitation [see Fig. 5(b)]. This behavior of the CT excitation can also be seen in the other blends and confirms this localized character.

III. CONCLUSION

Mixed films of ZnPC and F8ZnPc in different ratios were prepared. These were analyzed using photoluminescence, optical absorption, and electron energy-loss spectroscopy. The PL spectra of the blends substantially differ from the pure materials, and the emission in the blends is assigned to charge-transfer excited states in molecular pairs of ZnPC and F8ZnPc. Optical absorption reveals evidence for the related charge-transfer excitation. The fact that EELS data do not show the momentum dependence of the spectral onset corresponds well to the localized character of this charge-transfer excitation.

IV. METHODS

Thin mixed films were prepared by thermal evaporation under high vacuum (10^{-8} mbar). The film thicknesses were controlled using a quartz thickness monitor. With a total rate of about 0.16 \AA s^{-1} , 100 nm thick films were evaporated onto a KBr substrate kept at room temperature.

Optical spectroscopy was performed in the UV–vis range and in the IR range at 77 K and atmospheric pressure using a Bruker Vertex spectrometer equipped with a microscope. Photoluminescence (PL) measurements were carried out with a setup of a helium–cadmium laser with 325 nm excitation wavelength. The power was kept constant with a gray filter to $200 \mu\text{W}$. A grating monochromator in combination with a 2D-CCD camera was used to detect the photoluminescence. All PL measurements were executed

at 13 K using a closed helium circuit. Momentum dependent measurements of the excitation spectrum were performed using electron energy-loss spectroscopy (EELS). A high energy electron beam (172 keV) is transmitted through the sample and is scattered inelastically.^{38,39} Momentum values were chosen according to the electron diffraction profiles, so they do not correspond to Bragg peak positions. As high energy electrons can damage organic samples and to avoid thermal broadening, all measurements are performed at 20 K and in ultra-high vacuum. Besides the excitation spectra, EELS can also provide electron diffraction patterns, which allow us to draw conclusions about the structure of our thin films. We have compared the diffraction profiles to those of α - and β -ZnPC,^{40,41} showing that all of our evaporated ZnPC films are grown in the α -phase (see the [supplementary material](#)).

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for structural characterization with electron diffraction and IR data composition and phase information of the blends.

AUTHORS' CONTRIBUTIONS

L.G., K.O., K.L., and M.K. prepared the manuscript. L.G. and K.O. prepared the samples. L.G. and M.N. measured IR and UV-vis. L.G. and L.P.D. measured PL. J.B. and J.H. contributed to the PL data analysis. EELS measurements were done by L.G. All authors discussed the data and their interpretation.

ACKNOWLEDGMENTS

We are grateful to R. Hübel and F. Thunig for technical assistance. Financial support by the Deutsche Forschungsgemeinschaft within Project Nos. KN393/25, KN393/26, and LE747 is gratefully acknowledged. The publication of this article was funded by the Open Access Fund of the Leibniz Association.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

- 1 R. A. Street, D. Davies, P. P. Khlyabich, B. Burkhardt, and B. C. Thompson, *J. Am. Chem. Soc.* **135**, 986 (2013).
- 2 M. Schwarze, W. Tress, B. Beyer, F. Gao, R. Scholz, C. Poelking, K. Ortstein, A. A. Günther, D. Kasemann, D. Andrienko, and K. Leo, *Science* **352**, 1446 (2016).
- 3 H. Brinkmann, C. Kelting, S. Makarov, O. Tsaryova, G. Schnurpfeil, D. Wöhrle, and D. Schlettwein, *Phys. Status Solidi A* **205**, 409 (2008).
- 4 J. Meiss, A. Merten, M. Hein, C. Schuenemann, S. Schäfer, M. Tietze, C. Uhrich, M. Pfeiffer, K. Leo, and M. Riede, *Adv. Funct. Mater.* **22**, 405 (2012).
- 5 C. W. Tang, *Appl. Phys. Lett.* **48**, 183 (1986).
- 6 T. Stübinger and W. Brütting, *J. Appl. Phys.* **90**, 3632 (2001).
- 7 P. Peumans, A. Yakimov, and S. R. Forrest, *J. Appl. Phys.* **93**, 3693 (2003).
- 8 M. Riede, T. Mueller, W. Tress, R. Schueppel, and K. Leo, *Nanotechnology* **19**, 424001 (2008).

- 9 S. A. Van Slyke, C. H. Chen, and C. W. Tang, *Appl. Phys. Lett.* **69**, 2160 (1996).
- 10 S. Hammer, T. Ferschke, G. V. Eyb, and J. Pflaum, *Appl. Phys. Lett.* **115**, 263303 (2019).
- 11 M. Brendel, S. Krause, A. Steindamm, A. K. Topczak, S. Sundarraj, P. Erk, S. Höhla, N. Fruehauf, N. Koch, and J. Pflaum, *Adv. Funct. Mater.* **25**, 1565 (2015).
- 12 M. Knupfer and H. Peisert, *Phys. Status Solidi A* **201**, 1055 (2004).
- 13 A. Opitz, B. Ecker, J. Wagner, A. Hinderhofer, F. Schreiber, J. Manara, J. Pflaum, and W. Brütting, *Org. Electron.* **10**, 1259 (2009).
- 14 A. Opitz, J. Wagner, W. Brütting, A. Hinderhofer, and F. Schreiber, *Phys. Status Solidi A* **206**, 2683 (2009).
- 15 A. Hinderhofer and F. Schreiber, *ChemPhysChem* **13**, 628 (2012).
- 16 K. Yamada, S. Yanagisawa, T. Koganezawa, K. Mase, N. Sato, and H. Yoshida, *Phys. Rev. B* **97**, 245206 (2018).
- 17 M. Schwarze, K. S. Schellhammer, K. Ortstein, J. Benduhn, C. Gaul, A. Hinderhofer, L. P. Toro, R. Scholz, J. Kublitski, S. Roland, M. Lau, C. Poelking, D. Andrienko, G. Cuniberti, F. Schreiber, D. Neher, K. Vandewal, F. Ortman, and K. Leo, *Nat. Commun.* **10**, 2466 (2019).
- 18 P. R. Warren, J. F. M. Hardigree, A. E. Lauritzen, J. Nelson, and M. Riede, *AIP Adv.* **9**, 035202 (2019).
- 19 R. Warren, A. Privitera, P. Kaienburg, A. E. Lauritzen, O. Thimm, J. Nelson, and M. K. Riede, *Nat. Commun.* **10**, 5538 (2019).
- 20 M. Szybowicz, T. Runka, M. Drozdowski, W. Bała, M. Wojdyła, A. Grodzicki, P. Piszczek, and A. Bratkowski, *J. Mol. Struct.* **830**, 14 (2007).
- 21 M. M. El-Nahass, H. M. Zeyada, M. S. Aziz, and N. A. El-Ghamaz, *Opt. Mater.* **27**, 491 (2004).
- 22 W. Bała, W. M. Wojdyła, M. Rębarz, M. Szybowicz, M. Drozdowski, A. Grodzicki, and P. Piszczek, *J. Optoelectron. Adv. Mater.* **11**, 264 (2009); available at https://www.researchgate.net/publication/255698291_Influence_of_central_metal_atom_in_MPC_M_Cu_Zn_Mg_Co_on_Raman_FT-IR_absorbance_reflectance_and_photoluminescence_spectra
- 23 M. Wojdyła, B. Derkowska, Z. Lukasiak, and W. Bała, *Mater. Lett.* **60**, 3441 (2006).
- 24 E. A. Lucia and F. D. Verderame, *J. Chem. Phys.* **48**, 2674 (1968).
- 25 M. Kasha, *Radiat. Res.* **20**, 55 (1963).
- 26 I. V. Bondarev, A. Popescu, R. A. Younts, B. Hoffman, T. McAfee, D. B. Dougherty, K. Gundogdu, and H. W. Ade, *Appl. Phys. Lett.* **109**, 213302 (2016).
- 27 D. Schlettwein, K. Hesse, N. E. Gruhn, P. A. Lee, K. W. Nebesny, and N. R. Armstrong, *J. Phys. Chem. B* **105**, 4791 (2002).
- 28 H. Peisert, M. Knupfer, and J. Fink, *Appl. Phys. Lett.* **81**, 2400 (2002).
- 29 M. Pope and C. E. Swenberg, *Electronic Processes in Organic Crystals and Polymers* (Oxford University Press, 1999).
- 30 G. A. Kumar, J. Thomas, N. V. Unnikrishnan, V. P. N. Nampoori, and C. P. G. Vallabhan, *J. Porphyrins Phthalocyanines* **5**, 456 (2001).
- 31 L. Bajema, M. Gouterman, and B. Meyer, *J. Mol. Spectrosc.* **27**, 225 (1968).
- 32 J. Savolainen, D. van der Linden, N. Dijkhuizen, and J. L. Herek, *J. Photochem. Photobiol., A* **196**, 99 (2008).
- 33 C. Murray, N. Dozova, J. G. McCaffrey, N. Shafizadeh, W. Chin, M. Broquier, and C. Crépin, *Phys. Chem. Chem. Phys.* **13**, 17543 (2011).
- 34 L. Edwards and M. Gouterman, *J. Mol. Spectrosc.* **33**, 292 (1970).
- 35 R. Schuster, M. Knupfer, and H. Berger, *Phys. Rev. Lett.* **98**, 037402 (2007).
- 36 F. Roth, M. Nohr, S. Hampel, and M. Knupfer, *Europhys. Lett.* **112**, 37004 (2015).
- 37 M. Naumann and M. Knupfer, *J. Chem. Phys.* **149**, 084704 (2018).
- 38 F. Roth, A. König, J. Fink, B. Büchner, and M. Knupfer, *J. Electron Spectrosc. Relat. Phenom.* **195**, 85 (2014).
- 39 J. Fink, *Adv. Electron. Electron Phys.* **75**, 121 (1989).
- 40 S. Senthilarasu, R. Sathyamoorthy, and S. K. Kulkarni, *Mater. Sci. Eng. B* **122**, 100 (2005).
- 41 S. Senthilarasu, Y. B. Hahn, and S.-H. Lee, *J. Appl. Phys.* **102**, 043512 (2007).