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A nitrophenyl-carbazole based push-pull linker as a building block for non-linear optical active coordination polymers: A structural and photophysical study

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ABSTRACT

Non-linear optical effects (NLO) such as multi-photon absorption, second harmonic generation (SHG) etc. have a wide range of applications. Nevertheless, the performance of many NLO-active organic dyes is limited by their thermal stability and photobleaching. These problems can be overcome by integrating the dyes into coordination polymers or metal-organic frameworks. Here, we present a structural and photophysical study of dipropyl-9-(4-nitrophenyl)-carbazole-3,6-dicarboxylate, a new "push-pull" organic dye molecule designed as a chromophore linker for NLO-active coordination polymers. Structure determination of a single-crystal showed that it crystallizes in a monoclinic crystal system $P 2_1/c$. The solvated chromophore exhibits two aromatic absorption bands at 250 nm and 275 nm as well as broad long wavelength band at 350 nm, which we assign to an intramolecular charge transfer state. Photoluminescence measurements in solvents of different polarities revealed two main effects: In nonpolar solvents, the spectrum shows an emission band at 360 nm, whereas in solvents with a higher polarity, the emission maximum broadens and redshifts. Solid-state emission measurement of sample powder exhibits an emission band at 520 nm which is redshifted compared to the measurements in solution, due to excimer formation in the solid-state. The optical as well as solvation-related properties of the investigated pigment render it to be a versatile ligand in coordination polymers.

1. Introduction

Coordination polymers (CPs) and metal-organic frameworks (MOFs) featuring chromophore linkers as building blocks have been recognized as a promising solid-state material class for non-linear optical (NLO) applications, as their high chemical tunability, among other effects, enables to organize chromophore molecules in a defined oriented fashion [1].

To date, NLO studies on CPs and MOFs have been focusing on second- and third-harmonic generation (SHG, THG) as well as multi-photon absorption (MPA) properties [2–5]. These studies follow a common strategy, to assemble small NLO active organic building blocks in achieving highly functional crystalline solid-state materials, meanwhile surpassing often found drawbacks with classical NLO materials (e.g. limited performance, toxicity, photostability, non-polar arrangements etc.) [6,7]. Such an approach, however, requires comparatively small NLO-active chromophore linker molecules, with the desired optical properties and good crystallization tendencies.

NLO properties of chromophores have systematically been investigated within the electronic push-pull concept [8], which reveals a strong correlation between both the NLO-activity and the intramolecular charge transfer (ICT) characteristics and the size or structure of the charge transfer network. The NLO response was shown to be tailored by (i) connecting electron donors and acceptors of various electronic nature, (ii) assuring efficient donor-acceptor interaction (iii) extent, composition and steric arrangement of π -electron bridges (iv) reduction

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of the bond-length alternation of the π -bridges and (v) planarization of the π -electron system [8,9].

In general, the photophysical (including NLO) properties of coordination polymers can be influenced by each of their components - both the organic linkers as well as the metal nodes as well as the excitonic coupling between the linker molecules [10]. For example, photoactive ions capable of metal-centered transitions can be used, e.g. lanthanides, steering the photophysical properties of the material solely by choice of the metal [11]. Often the situation is more complex, exhibiting a delicate interplay of (also photo-inactive) metal ions, especially transition metal ions, and chromophore linkers. Hereby, metal-to-ligand charge transfer (MLCT) as well as ligand-to-metal charge transfer (LMCT) can introduce new charge transfer bands, which possibly allow for a higher NLO response of the material compared to the isolated linker. As stated above, the emission properties of organic chromophores are well understood and can be specifically tailored towards desired applications. Therefore, tailoring the organic chromophores within linker platforms is also the method of choice for optimizing photoactive coordination compounds and networks. Additionally, there are two further advantages: First, the incorporation of linker molecules inside a framework usually increases their emission efficiency, through limitation of radiationless energy decays as a result of a restriction of conformational changes in the coordinated chromophore [12]. Second, by arranging the chromophores in a rigid framework a dense packing of the chromophores is enabled, whereas fluorescence quenching via aggregation (which is usually observed in highly concentrated solutions) is prevented [13]. Based on this, we identified dicarboxy-functionalized carbazoles as highly promising donor building blocks within the push-pull linker design of prospective NLO-photoactive coordination polymers or MOFs [14–16].

Herein, we report the synthesis and complete characterization of a new potential push-pull linker, comprising a carbazole donor and a -NO₂ acceptor group. Both are linked via a phenylene bridge, mimicking the well-studied showcase NLO chromophore *p*-nitroaniline (PNA) [17]. The carbazole moiety is equipped with carboxylic acid groups, which should enable an incorporation into framework structures. 9-(4-nitrophenyl)-carbazole-3,6-dicarboxylic acid (H2CbzNO2, 8) was synthesized in a multi-step procedure starting from carbazole. The molecule was characterized by NMR spectroscopy, mass spectrometry and elemental analysis. Single-crystal X-ray diffraction (SCXRD) analysis reveals an antiparallel packing motif, minimizing the overall dipole-moment of the unit cell, a behavior often found for polar molecules [18,19]. Finally, the absorption and emission behavior were studied in solution as well as in solid state. The spectroscopic findings were corroborated with the help of electronic structure calculations at the level of time-dependent density functional theory (TD-DFT). The spectroscopic results and the theoretical calculations show the formation of an ICT state, proving H₂CbzNO₂ as a highly prospective NLO ligand for future CP and MOF synthesis.

2. Experimental

2.1. Material and methods

All purchased reagents were received from chemical suppliers and used without any further purification if not otherwise stated. All reactions with air and moisture sensitive compounds were carried out under standard Schlenk techniques using Argon 4.6 (Westfalen) or in a glove box (*UNIlab*, M. Braun). Required glass ware was flame-dried *in vacuo* prior to use. Elemental analysis was performed at the micro analytic laboratory at the Technical University of Munich. Analysis of C, H and N values was conducted by flash combustion method at 1800 °C. NMR spectra were recorded on a Bruker AV400 at room temperature at 400 MHz. ESI-MS was performed on a *LCQ fleet* and *MS Q*⁺ from Thermo Fischer Scientific. LIFDI-MS spectra were measured at a Waters Micromass *LCT TOF* mass spectrometer equipped with an LIFDI ion source (LIFDI 700) from Linden CMS GmbH. Single-crystal X-ray diffraction data was collected on a BRUKER *D8 Venture* system equipped with a Mo TXS rotating anode ($\lambda = 0.71073$ Å) and a CMOS photon 100 detector. UV/VIS spectra were recorded on a double beam *Lambda 365* UV–Vis spectrophotometer from PerkinElmer. Fluorescence measurements were recorded on an *FS5* spectrofluorometer from Edinburgh Instruments. Cyclic voltammetry measurements were conducted on a BioLogic *SP-200*. Melting point analysis was performed on a Büchi *M-565*.

2.2. Computational methods

All quantum mechanical calculations were performed using the Gaussian09 software package [20]. The long-range corrected coulomb-attenuated exchange-correlation functional cam-B3LYP [21] and the basis set def2TZVP were employed as implemented in the software package. Theoretical absorption spectra were calculated on the level of time-dependent DFT using the above functional and basis set. No symmetry or internal coordinate constraints were applied during the optimization. The optimized geometry was verified as being a true minimum by the absence of negative eigenfrequencies in the vibrational frequency analysis.

2.3. Synthesis

3,6-Dibromocarbazole (2): A solution of *N*-bromosuccinimide (22.35 g, 125 mmol) in 50 mL DMF was slowly added through a syringe pump to a stirring solution of carbazole **1** (10 g, 59.80 mmol) in 20 mL DMF in an ice bath. After 24 h of reaction time, the mixture was poured into 600 mL ice water and then filtered through a suction filter to give a dark grey powder. The crude product was recrystallized with Ethanol to give a grey powder of 3,6-Dibromocarbazole **2** (18,68 g, 96%). ¹H NMR (400 MHz, 298K, DMSO-*d*₆) δ (ppm) = 7.47 (d, *J* = 8.6 Hz, 2H), 7.53 (dd, *J* = 2.0, 8.6 Hz, 2H), 8.43 (d, *J* = 1.9, 2H), 11.59 (s, 1H, N–H). ¹³C NMR (101 MHz, 298K, DMSO-*d*₆) δ (ppm) = 110.96, 113.18, 123.35, 123.29, 128.70, 138.78.

Carbazole-3,6-Dicarbonitrile (3): 3,6-Dibromocarbazole 2 (9.75 g, 30.0 mmol) and dppf (100 mg, 0.18 mmol) were added to a 100 mL Schlenk flask and solved in 30 mL DMF and 0.3 mL water. The suspension was degassed via bubbling argon for 1 h through the mixture. Subsequently, Zn(CN)2 (4.21 g, 36 mmol), zinc powder (78 mg, 1.2 mmol), Zn(OAc) $_2$ · 2 H₂O (0.26 g, 1.2 mmol) and Pd₂(dba) $_3$ · dba (69.5 mg, 0,06 mmol) were added under a positive pressure of argon. This mixture was heated to 110 °C for 2 days. The suspension was subsequently cooled and then poured into a 100 mL mixture of H₂O/NH₄Cl/ NH_3 (5/4/1) and filtered through a suction filter. The filter cake was washed with the same volume of the above mixture, toluene (3 x 30 mL) and MeOH (3 x 30 mL) to give a grey solid. The crude product was recrystallized with DMF to give a white solid (3) (5.2 g, 81%). ¹H NMR (400 MHz, 298K, DMSO- d_6) δ (ppm) = 7.72 (d, J = 8.5 Hz, 2H), 7.85 (d, J = 9.9 Hz, 2H), 8.80 (s, 2H), 12.38 (s, 1H, N–H). ¹³C NMR (101 MHz, 298K, DMSO- d_6) δ (ppm) = 101.74, 112.84, 120.10, 121.85, 126.8, 129.93, 142.32.

Carbazole-3,6-dicarboxylic acid (4): Carbazole-3,6-Dicarbonitrile **3** (4.2 g, 19.3 mmol) was suspended in an aqueous NaOH solution (12.45 g in 150 mL). To this solution CuI (37,5 mg, 0.195 mmol) was added and then quickly heated to 125 °C for 2 days, until the starting material was dissolved. Afterwards active carbon was added, and the mixture was again heated to 125 °C for 2 h. After cooling, the suspension was filtered through celite, which was pre-washed with aq. NaOH-solution. The filtrate was acidified with 6 M HCl-solution to give a white precipitate. The precipitate was filtered, washed with water and then dried to give a withe solid (4) (4.0 g, 85%). ¹H NMR (400 MHz, 298K, CDCl₃) δ (ppm) = 7.60 (d, *J* = 8.5 Hz, 2H), 8.06 (d, *J* = 8.4 Hz, 2H), 8.85 (s, 2H), 12.04 (s, 1H, N–H), 12.69 (bs, 2H, COOH). ¹³C NMR (101 MHz, 298K, DMSO-d₆) δ (ppm) = 111.13, 122.00, 122.27, 122.79, 127.65, 143.12, 167.94.

Dipropyl-carbazole-3,6-dicarboxylate (5): Carbazole-3,6-dicarboxylic acid 4 (4.0 g, 15.64 mmol) was suspended in 100 mL 1propanol. To this suspension, conc. sulfuric acid (2 mL) was added and then refluxed at 110 °C for 24 h. After cooling, the suspension was concentrated on a rotary evaporator and extracted with 200 mL dichloromethane. The organic layer was washed with aq. NaHCO₃ (150 mL) and then dried with MgSO₄. The solvent was evaporated to give a yellowish solid (5) (4.5 g, 84%). ¹H NMR (400 MHz, 298K, CDCl₃) δ (ppm) = 1.09 (t, J = 7.4 Hz, 6H), 1.87 (h, J = 7.2 Hz, 4H), 4.36 (t, J =6.7 Hz, 4H), 7.47 (d, J = 8.5 Hz, 2H), 8.18 (dd, J = 1.5 Hz, 2H), 8.86 (s, 2H). ¹³C NMR (101 MHz, 298K, CDCl₃) δ (ppm) = 10.77, 22.40, 66.67, 110.64, 122.89, 123.19, 128.28, 142.85, 167.35.

Dipropyl-9-(4-nitrophenyl)-carbazole-3,6-dicarboxylate (Pr₂CbzNO₂) (6): Dipropyl-carbazole-3,6-dicarbox-ylate 5 (0.87 g, 2.56 mmol), 1-iodo-4-nitrobenzene (0.638 g, 2.56 mmol), K₃PO₄ (2.18 g, 10.3 mmol), N,N'-dimethylethylenediamine (0.18 mL, 1.67 mmol) and CuI (73.15 mg, 0.39 mmol) were dissolved in 20 mL dry toluene in a 50 mL Schlenk flask and heated to 115 °C for 2 days. After cooling, the suspension was dissolved in 100 mL aq. NH₄Cl, extracted with EtOAc (3 x 50 mL). The organic phase was combined and then dried with MgSO₄. The solvent was evaporated on a rotary evaporator to give an orange solid. The crude product was then subjected to column chromatography (100% dichloromethane, $R_f = 0.75$) to give a yellow powder (843 mg, 72%). mp 227 °C; ¹H NMR (400 MHz, 298K, CDCl₃) δ (ppm) = 1.09 (t, J = 7.4 Hz, 6H), 1.88 (h, J = 6.7 Hz, 4H), 4.37 (t, J = 6.7 Hz, 4H), 7.46 (d, J = 8.7 Hz, 2H), 7.81 (d, 8.9 Hz, 2H), 8.20 (dd, J = 1.4 Hz, 2H), 8.54 (d, J = 8.9 Hz, 2H), 8.92 (s, 2H). ¹³C NMR (101 MHz, 298K, CDCl₃) δ (ppm) = 1.16, 10.75, 22.37, 66.86, 109.65, 123.30, 123.90, 124.39, 125.94,127.45, 128.76, 143.35, 166.86. LIFDI-MS: *m/z* [M]^{•+}: calculated for C₂₆H₂₄O₆N₂: 460.16; found: 459.55. EA: calculated for C₂₆H₂₄O₆N₂: C, 67.82; H, 5.25; N, 6.08; found: C, 67.35; H, 5.27; N, 5.87.

Dipropyl-9-(4-phenyl)-carbazole-3,6-dicarboxylate (Pr₂CbzH) (7): Dipropyl-carbazole-3,6-dicarboxylate (0.3 g, 0.88 mmol), iodobenzene (0.18 g, 0.88 mmol), K₃PO₄ (0.750 g, 3.54 mmol), DMEDA (0.06 mL, 0,58 mmol) and CuI (25.5 mg, 0.13 mmol) were dissolved in 10 mL dry toluene in a 50 mL Schlenk flask and heated to 115 °C for 3 days. After cooling, the suspension was dissolved in 60 mL aq. NH₄Clsolution, extracted with EtOAc (4 x 30 mL). The organic phase was combined and then dried with MgSO₄. The solvent was evaporated on a rotary evaporator, to give a brown solid. The crude product was then subjected to column chromatography (100% dichloromethane, $R_f = 0.8$) to give a white powder (6) (295 mg, 80%). mp 133 °C; ¹H NMR (400 MHz, 298K, CDCl₃) δ (ppm) = 1.09 (t, J = 7.4 Hz, 6H), 1.88 (h, J = 6.7 Hz, 4H), 4.37 (t, J = 6.7 Hz, 4H), 7.46 (d, J = 8.7 Hz, 2H), 7.81 (d, 8.9 Hz, 2H) 8.20 (dd, J = 1.4 Hz, 2H), 8.54 (d, J = 8.9 Hz, 2H), 8.92 (s, 2H). ¹³C NMR (101 MHz, 298K, CDCl₃) δ (ppm) = 1.16, 10.75, 22.37, 66.86, 109.65, 123.30, 123.90, 124.39, 125.94, 127.45, 128.76, 143.35, 166.86. EA: calculated for C₂₆H₂₅O₄N: C, 75.16; H, 6.07; N, 3.37; found: C, 74.99; H, 6.07; N, 3.52.

9-(4-nitrophenyl)-carbazole-3,6-dicarboxylic acid (H₂CbzNO₂) (8): Dipropyl-9-(4-nitrophenyl)-carbazole-3,6-dicarboxylate (500 mg, 1.2 mmol) was dissolved in 50 mL THF, aq. NaOH-solution (0.25 g in 10 mL water) and 7.5 mL MeOH. This mixture was refluxed for 12 h at 90 °C. After cooling, the solvent was evaporated and 100 mL water was added. The suspension was filtered and subsequently acidified with 3 м HCl-solution. The precipitate was filtered, washed thoroughly with water and then dried, to give a yellow solid (310 mg, 84%). ¹H NMR $(400 \text{ MHz}, 298\text{K}, \text{DMSO-}d_6) \delta (\text{ppm}) = 7.59 (\text{d}, J = 9.0 \text{ Hz}, 2\text{H}), 8.04 (\text{d}, \text{d})$ *J* = 9.0 Hz, 2H), 8.11 (dd, *J* = 1.6 Hz, 8.7 Hz, 2H), 8.55 (d, *J* = 9.0 Hz, 2H), 9.00 (s, 2H), 12.89 (bs, 2H, COOH). ¹³C NMR (101 MHz, 298K, DMSO- d_6) δ (ppm) = 110.12, 123.07, 123.11, 124.18, 125.76, 127.85, 128.49, 141.69, 142.76, 146.44, 167.48. ESI-MS: m/z [M - H]: calculated for C₂₀H₁₂O₆N₂: 375.313; found: 375.14. EA: calculated for C₂₀H₁₂O₆N₂ · 0.75 H₂O: C, 61.62; H, 3.49; N, 7.19; found: C, 61.80; H, 3.47; N, 7.02.

9-(4-phenyl)-carbazole-3,6-dicarboxylic acid (H2CbzH) (9): The

literature known compound 9-(4-phenyl)-carbazole-3,6-dicarboxylic acid [22] was synthesized in a saponifaction reaction, using the analogous reaction conditions to that described for **8**. ¹H NMR (400 MHz, 298K, DMSO- d_6) δ (ppm) = 7.43 (d, J = 8.7 Hz, 2H), 7.58–7.79 (m, 5H), 8.10 (dd, J = 1.6 Hz, 8.7 Hz, 2H), 8.98 (s, 2H), 12.82 (bs, 2H). ¹³C NMR (101 MHz, 298K, DMSO- d_6) δ (ppm) = 109.87, 122.46, 123.01, 123.36, 127.00, 128.27, 128.65, 130.40, 135.78, 143.49, 167.62.

3. Results and discussion

3.1. Synthesis

The dipolar push-pull chromophore dipropyl-9-(4-nitrophenyl)carbazole-3,6-dicarboxylate (Pr₂CbzNO₂) 6 was synthesized in a six step synthesis procedure starting from carbazole 1 (Fig. 1). Bromination of 1 yielded 3,6-dibromocarbazole 2, which was subsequently reacted to carbazole-3,6-dicarbonitrile 3 in a modified Negishi coupling reaction [23,24]. Alkaline hydrolysis of **3** followed by acidic precipitation gave 3, 6-carbazole-dicarboxylic acid 4. It turned out that the low solubility and acidic behavior of 4 hampered N-hetero cross-coupling reactions of Buchwald-Hartwig or Ullman type. Consequently, to enhance the solubility of the carbazole donor precursor 4, the corresponding propyl ester 5 was synthesized in an acid-catalyzed esterification reaction. Furthermore, different Ullmann and Buchwald-Hartwig coupling reaction attempts were screened under varying reactions conditions finally yielding the desired product 6 (compare the experimental part for a detailed procedure). A modified Ullmann reaction procedure following work by Eddaoudi et al. results in high yield and excellent purity [25]. As the compound should be used as a building block for CP synthesis in pursuing work, 6 was hydrolyzed by alkaline esterification finally giving the corresponding carboxylic acid 8. Please note that all optical characterization methods discussed in the following paragraphs were conducted on 6 due to the higher solubility of the latter in differing organic solvents. The effects of the propyl ester group of 6 on optical properties are marginal, as the absorption and emission behavior are determined by the push-pull system, as will be shown in the following paragraphs.

3.2. Photophysical characterization in solution

3.2.1. UV/VIS spectroscopy

The photophysical properties of **6** were studied using UV/Vis spectroscopy in solvents of different polarity (Fig. 2a). In all solvents the absorption spectra show two strong absorption bands centered at 250 nm and 275 nm, as well as weaker bands around 300 nm and a characteristic broad absorption band centered at approximately 355 nm. We pursue two strategies to assign the origin of these spectral features: *i*) comparison with the spectra of the reference compound dipropyl-9-(4-phenyl)-carbazole-3,6-dicarboxylate (Pr₂CbzH) **7** (Fig. 2, yellow), and *ii*) comparison with quantum chemical calculations of the absorption spectrum.

Compound **6** and the reference **7** differ in molecular structure only by the *p*-nitro group (Fig. 2c), which implies that any spectral differences report on the influence of the nitro acceptor group on the molecular photophysics of the push-pull chromophore. The similarity of the shortwavelength range of the spectra suggest that the features below 300 nm can be assigned to π - π * transitions located at the carbazole moiety. In the long-wavelength range, however, we observe significant differences. In particular, the absorbance spectra of **7** have only minor bands redshifted with respect to the π - π * transitions (Fig. 2). Thus, the longwavelength band at **6** is clearly induced by the electron accepting $-NO_2$ group. While introducing electron-withdrawing groups may result in charge-transfer transitions, the modest solvatochromy of the band shows that these transitions are associated with only a minor change in permanent dipole moment.

To obtain further insight into the electronic structure of **6**, and to corroborate our assignments of the spectroscopic data, we perform a

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Fig. 1. Reaction scheme for the preparation of 8 (and 9) showing the different conducted steps from commercially available starting materials.



Fig. 2. a) Side-by-side comparison of the absorbances of **6** in different solvents with increasing polarity, from toluene to ethanol, as well as **7** in DCM. b) Zoom-in of the outlined area (dashed box) in the left panel focusing on the absorption of the charge transfer state. c) Molecular structure of chromophores **6** and **7**.

quantum chemical analysis of the compound's absorption spectra. This was done at the level of TD-DFT using the long-range corrected cam-B3LYP functional and def2TZVP as basis set (50 excited states, Fig. 3).

The calculated UV/VIS spectrum is in good accordance with the experimental absorbance spectrum and shows two main groupings of transitions in the UV region centered at 180 nm and 240 nm. Qualitative (visual) comparison of the most contributing Kohn-Sham molecular orbitals (KS-MOs) of these excitations show that these transitions are mostly of π - π * character and located at the carbazole moiety (not shown). The band at approximately 310 nm however, involves substantial transfer of charge-density towards the nitrobenzene moiety, and the $S_0 \rightarrow S_1$ transition can thus be assigned to a charge-transfer excitation. Fig. 3b shows the KS-MOs most strongly involved in the S_1 transition, where the transfer of electron density from the donating carbazole to the

electron accepting nitro group upon photo excitation is clearly illustrated.

3.2.2. Photoluminescence and excitation spectroscopy

To unravel the emission properties of this new organic chromophore, we conducted a detailed photoluminescence (PL) spectroscopic investigation. Excitation-emission-matrices (EEM) of **6** were measured in order to study the excitation-wavelength dependent fluorescence behavior in different polar surroundings (Fig. 4). The collected data point towards a subtle interplay of a locally excited (LE) state at the carbazole moiety and a twisted intramolecular charge-transfer (TICT) state involving the carbazole donor and nitro acceptor as a function of solvent polarity (Fig. 5). The EEMs reveal the formation of two contributions. In solvents of low polarity (toluene, Fig. 4a) the spectra show a



Fig. 3. a) Theoretical UV/VIS spectrum of 6 (50 excited states, gaussian broadening) b) Charge transfer excitation of 6 located from the carbazole moiety to the phenyl ring (S1, 310 nm, oscillator strength f, transition dipole moment tdm [D], HOMO (left) \rightarrow LUMO (right)).



Fig. 4. Excitation-emission-matrices (EEM) of 6 in different solvents: a) toluene, b) THF, c) DCM, d) MeCN and e) EtOH as well as 7 in DCM for comparison, f). Note the different scaling of the x/y axis for clarity reasons.



Fig. 5. A pictorial description of the interplay between LE and CT states in the push-pull chromophore **6** and how the solvent reaction field shapes the excited state PES. a) In non-polar solvents, the lowest state will hold π - π * character. b) In more polar solvents the TICT state will be lowered due to stabilization by the reaction field, resulting in an equilibration with the LE state. c) Finally, at strong-polar solvents the TICT state gets close to the S₀ surface, resulting in a large increase in non-radiative relaxation, preventing its contribution to emission.

single emissive state, with a PL maximum at \sim 360 nm. By increasing the solvent's polarity, an additional emission band appears which redshifts and broadens distinctively (\sim 430 nm in THF, Fig. 4b; \sim 570 nm in DCM). Finally, in very polar and protic solvents such as ethanol, the long-wavelength contribution vanishes (Fig. 4d and e). The EEMs show no long-wavelength contribution to the emission signal, and the spectra are remarkably similar to the spectra in low-polar solvents. To gain further insights, we also measured an EEM of 7, following a similar strategy as presented in the UV/Vis spectroscopic studies with the aim to understand the influence of the –NO₂ substituent. Interestingly, the EEM of 7 in DCM reveal two emission bands, with lowest-energy transitions at (\sim 290 nm) and (\sim 360 nm), respectively.

Taken the above into consideration, the dual-emission behavior of **6** can be understood within a TICT-model. In less polar solvents the lowest energy state will show LE character with a narrow PL band and a maximum at approximately 360 nm. Via comparison of EEMs of **6** and **7** displayed in Fig. 4, we assign this LE state to be largely located at the carbazole moiety. However, in more polar surroundings TICT states will be stabilized, due to the increased dipole moment through twisting of the chromophore alongside the C–N single bond. Consequently, the TICT state will contribute stronger to the emission band - which is most pronounced in DCM. Finally, in very polar and protic surroundings (here acetonitrile and ethanol) the TICT state is potentially lowered to a strong extent, with the typical reduction in transition moment due to the

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extensive charge-separation, likely leading to essentially complete quenching of the TICT emission. Instead, the EEMs clearly show that only the LE emission remains in these cases. Fig. 5 displays the interplay of LE and TICT states of **6** in different polar surroundings. Note that such an approach of describing the excited state dynamics is commonly used for push-pull chromophores [26–28]. In summary, the static excitation and emission spectroscopic analysis of **6** reveals a highly interesting photophysical behavior of the linker molecule, in particular showing a strong dependency on the polarity of the chromophore environment. Presumably, these effects can be exploited further in sensor systems (e. g., guest molecule detection) through controlled chromophore packing in a coordination polymer.

3.3. Crystal structure analysis

Single crystals suitable for single crystal X-ray diffraction (SCXRD) analysis were obtained by slow diffusion of pentane into a concentrated solution of 6 in chloroform. Fig. 6a shows the molecular structure of 6 and its packing along the crystallographic a and b-axis (Fig. 6b and c). The material crystallizes in the monoclinic space group $P 2_1/c$ with a single molecule of 6 in the asymmetric unit and four molecules per unit cell (Z = 4). The mean bond lengths found for the molecular structure from SCXRD analysis lay in ranges as expected for organic molecules of such types (Table S1). The carbazole unit and the nitrophenylene group hold a torsional angle of 52.50°. Interestingly, the -NO₂ group and the phenylene ring have a dihedral angle of almost 0°, proofing both molecule fragments to lay in a single plane. As can nicely been seen in Fig. 6b, the polar molecule crystallizes diametral in the ac-plane, minimizing the overall dipole moment of the unit cell. Furthermore, the molecule propagates along the crystallographic b-axis in a co-planar fashion, with a mean center-to-center distance of \sim 3.4 Å. Additional intermolecular hydrogen bonds of the type $C_{\text{arom}}\text{-}H\text{-}\text{-}O$ involving the ester group and the nitrophenylene group with characteristic distances ranging from 2.4 Å to 2.8 Å, contribute to the overall packing as found in the crystal structure. In summary, the SCXRD analysis reveals that the packing motif of 6 is mainly governed by electrostatic as well as intermolecular interactions (minimization of dipole moments, π - π interactions of the carbazole moiety and Carom-H---O interactions).

3.4. Solid-state photoluminescence and excitation spectroscopy

In order to characterize the photophysical properties in the solidstate, powder samples of 6 were investigated with solid-state

fluorescence and excitation spectroscopy. Fig. 7a shows the emission spectrum measured at different excitation wavelengths (280 nm and 425 nm, respectively) with an emission band located at 540 nm for both excitations. This is different, compared to the photoluminescence measurements in solution, where two emission bands can be seen: a LE band at 360 nm, as well as a solvent dependent red-shifting ICT. Furthermore, the solid-state spectrum shows two contributing transitions, as apparent from the excitation spectrum (red line in Fig. 7a), which we assign to carbazole based π - π * transitions (280 nm) and the charge transfer state (425 nm). To support our assignments, we also measured emission and excitation spectra for powdered 7 and compared it to 6 (Fig. 7b). Interestingly, 7 shows very similar emission - centered at 520 nm- but the excitation spectrum reveals only one absorptive transition. Based on these findings and the packing of the carbazole moieties into dimers with a distance of \sim 3.4 Å in the crystal structure, the solid-state emission of 6 (and 7) appears to originate from a π -stacked sandwich excimer formation, which has been observed 2001 in photoluminescence studies on carbazole dimers [29].

For a future incorporation of the chromophore in a CP, a similar effect can be expected, since a high chromophore density without fluorescence quenching should be achievable. On top, an additional advantage of these coordination materials compared to the crystallized linker itself is, that the photophysical properties can be potentially controlled via defined arrangement of the chromophores, whereas this is intrinsically limited in an organic crystal. This leads to a remarkable enlargement of the playfield of organic chromophores, deliberately packed and arranged in solid-state materials, thereby steering the photophysical properties of the solid-state material.

4. Conclusions

In conclusion, we have synthesized a novel dipolar "push-pull" chromophore dipropyl-9-(4-nitrophenyl)-carbazole-3,6-dicarboxylate via an modified *Ullmann*-coupling reaction, which should be used in further studies for the synthesis of NLO active CPs and MOFs. The chromophore was characterized by ¹H NMR and ¹³C NMR spectroscopy, LIFDI-MS and elemental analysis as well as SCXRD. The optical studies of chromophore **6** in solution showed two aromatic absorption bands at 250 nm and 275 nm as well as a broad long wavelength absorption band at 350 nm with characteristics of an ICT transition. The PL measurements in solvents of differing polarity, revealed an interesting interplay between locally excited states, centered at the carbazole moiety, and a twisted intramolecular charge transfer state between the carbazole



Fig. 6. Hydrogen atoms are omitted for clarity. **a)** ORTEP representation of the single-crystal structure of **6** with thermal ellipsoids shown at the 50% probability level. **b)** Alternating packing of **6** alongside the a/c plane. **c)** Co-planar packing of **6** alongside the b/c plane with a mean chromophore distance of 3.367 Å.



Fig. 7. a) Solid-State emission (blue and yellow line, $\lambda_{ex} = 280$ nm, 425 nm) and excitation spectrum (red line, $\lambda_{em} = 600$ nm) of **6.** b) Solid-State emission (yellow line, $\lambda_{ex} = 240$ nm) and excitation spectrum (red line, $\lambda_{em} = 520$ nm) of **7.** (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

donor and the nitro acceptor group. The solid-state emission measurements exhibited **6** as a greenish emitter with contributions from π -stacked excimer formation. Taking all these photophysical properties in account, the newly synthesized dipolar "push-pull" chromophore presents itself as a highly interesting building block to study within a structural-photophysical-property-relationship investigation on potential NLO active CPs or MOFs in the future.

Author contributions

Conceptualization and writing - original draft preparation, S.J.W., methodology, S.J.W., D.C.M., E.T. and A.P., writing – review and editing, D.C.M., E.T., J.H., A.P. and R.A.F., project administration, R.A.F. All authors have given approval to the final version of the manuscript.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2020.109012.

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