Anadolu Üniversitesi Bilim ve Teknoloji Dergisi A- Uygulamalı Bilimler ve Mühendislik
Anadolu University Journal of Science and Technology A- Applied Sciences and Engineering

ANADOLU UNIVERSITY

2017 - Volume: 18 Number: 5
Page: 1000 - 1007
DOI: 10.18038/aubtda.332785
Received: 04 August 2017 Accepted: 03 October 2017

SYNTHESIS AND CHARACTERIZATION OF NOVEL 4-CYNANOPHENYL-FUNCTIONALIZED N4,N4,N4′,N4′-TERAPHENYLBENZIDINE (TPB) AS HOLE TRANSPORTING MOLECULAR MATERIALS

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ABSTRACT

In this study, a new cyanophenyl-functionalized N4,N4,N4′,N4′-tetraphenylbenzidine (TPB) containing employable hole-transporting components has been synthesized with Pd-catalyzed Suzuki-Miyaura cross coupling reaction. N4,N4,N4′,N4′tetrakis-(4′-cynobiphenyl-4-yl)-biphenyl-4,4′-diamine (TPB-CN) was well characterized by 1H NMR, 13C NMR and CHN elemental analysis. The compound TPB-CN exhibited good thermal stability and luminescence properties. Time Dependent Density Functional Theory (TDDFT) computation was carried out to investigate the structural parameters and understand the photophysical properties of the novel TPB-CN compound. The experimental and theoretical calculations performed to calculate absorption maxima in DCM by UV-Vis and TD-B3LYP/6-31g(d,p) were compared with each other. To identify crystal structure and determine optical band gap of TPB-CN compound, its film form coated on the glass substrate by spin coating was used. The band gap of TPB-CN compound both in film and in solution was determined from the optical absorption measurements.

Keywords: N4,N4,N4′,N4′-tetraphenylbenzidine (TPB), Suzuki-Miyaura cross-coupling, Organic semiconductor, TDDFT, optical band gap

1. INTRODUCTION

Organic electronics have made a major development in the last twenty years changing its appearance to fit the futuristic devices that are ultrathin, comprise a wider range and are far more adjustable to certain needs including organic field-effect transistors (OFET), organic light emitting diodes (OLEDs) and organic photovoltaic's (OPVs). Thanks to processes during their fabrication that make them low in cost and low energy consuming, the old fashioned technologies based on inorganic materials will be soon to be replaced by the fascinating and dynamic technologies of organic electronics [1-3].

The hole transporting materials (HTMs) have been widely used in organic electronics including the devices such as OLED [4], OFET [5] and dye sensitized solar cells (DSSC) [6]. One of the most important HTMs is N4,N4,N4′,N4′-tetraphenylbenzidine (TPB in short) which is also named as triphenylamine dimer TAD or TPD [7-10] with a vital role in the organic electronics devices. Alternatively, they can also be used to building blocks, which constitute largely conjoined HTM molecules [11-13]. It can be claimed that the palladium-catalysed Suzuki Miyaura (SM) pairing reaction serves as the best method and the essential power tool for constituting biaryls. During this reaction there is a coupling of organic halides which are mainly a bromide with organoboron compounds present with a base and a catalytic amount of palladium complex. Low-temperature transmetalation reactions are frequently used to synthesize arylboronic acids and modifying or isolating them is nearly difficult. Therefore, they are purchased commercially, although they are expensive to use in SM couplings and restricting the scope of the parallel synthetic process [14-17]. Besides, arylboronic acids have some advantages such as avoiding the use of a strong base and the necessity for preformation of air-temperature-sensitive reagents [18-19].

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Considering the information in the literature the palladium-catalyzed Suzuki-Miyaura (SM) coupling reaction was carried out by using N4,N4,N4′,N4′-tetrakis-(p-bromophenyl)-biphenyl-4,4′-diamine (TPB-Br) and aryl boronic acid (Scheme 1). The N4,N4,N4′,N4′-tetraphenylbenzidine (TPB) derivatives are excellent non-planar donor molecules. Also these molecules are known as propeller-shaped, electron-rich, dimeric triphenylamine (TPA) [20]. The cyano group is an electron-withdrawing group and also it plays an important role to lower the HOMO levels [21].

In this paper, the HOMO-LUMO band gap levels of novel synthesized cyanophenyl-functionalized N4,N4,N4′,N4′-tetraphenylbenzidine (TPB-CN) derivative employable as hole-transporting molecular material is reported. In order to characterize the structures of TPB-Br and TPB-CN compounds well, the elemental analysis, 1H NMR, and 13C NMR spectroscopies have been used. TPB-CN film was coated on glass substrates to investigate the crystal structure and band gap of the TPB-CN compound. The new TPB-CN compound exhibited a good electron-donating ability and reasonably high thermal stability.

2. EXPERIMENTAL

2.1. Materials and Instruments

All reagents and solvents were purchased commercially and used without any purification. 1H and 13C NMR spectra were obtained from spectrometers Bruker DPX FT NMR (500 MHz) and (125 MHz) at 298 K (Germany). TMS ($CDCl_3$) as the internal reference and the chemical shifts were given in δ (ppm) relative. UV–vis absorption and fluorescence spectra were recorded respectively by Shimadzu UV2450 UV-vis scanning spectrometer and Perkin-Elmer LS-55 spectrophotometer fluorescence spectrometer. TG and DTA analyses were obtained with a Perkin Elmer Diamond TG/DTA Thermal Analyzer under a platinum pan using dry air. DSC measurements were measured on a DSC 2010 instrument in dry air, heating from 50 to 280 °C at 10 °C min^{-1} rate and cooling from 280 to 50 °C at 40 °C min^{-1} rate and then again heating from 50 to 280 °C at 10 °C min^{-1} rate. D2 Phaser Bruker X-Ray Automatic Diffractometer was used to get X-ray diffraction (XRD) patterns of coated TPB-CN film. The incident wavelength was 1.54059 Å in the XRD measurements taken at room temperature.

2.2. Synthesis

2.2.1. N4,N4,N4′,N4′-tetrakis-(p-bromophenyl)-biphenyl-4,4′-diamine (TPB-Br)

4,4′-Bis[(4-bromophenyl)phenylamino]biphenyl (0.1 g, 0.15 mmol) and N-bromosuccinimide (0.06 g, 0.371 mmol) were stirred in DMF (15 ml), at room temperature. N-bromosuccinimide solution was added dropwise while stirring the 4,4′-Bis[(4-bromophenyl)phenylamino]biphenyl solution, the color of the reaction mixture turned to light yellow. The reaction was stirred for 2 hours at room temperature, the reaction mixture was poured into water and then it was extracted with diethyl ether. After the extraction, the organic fractions were dried over anhydrous Na_2SO_4 and then filtered. The extracted solvent was evaporated in vacuo, then recrystallized in methanol to get a write solid with 90% yield (0.09 g). 1H NMR ($CDCl_3$, 500MHz): 6.99 (d, *J*=9Hz, 8H), 7.11 (d, *J*=9 Hz, 4H), 7.38 (d, *J*=9 Hz, 8H), 7.47 (d, *J*=9 Hz, 4H).

2.2.2. N4,N4,N4′,N4′tetrakis-(4′-cynobiphenyl-4-yl)-biphenyl-4,4′-diamine (TPB-CN)

4-Cyanophenylboronic acid (0,08g, 2.2 eq), TPB-Br (0.10 g, 1 eq), K_2CO_3 (2 M, 0.5 mL), tetrakis(triphenylphosphine) palladium 3 mol% and THF (10 ml) were placed in a round-bottomed flask with a magnetic stirrer. The mixture was refluxed under a N_2 atmosphere for 5 hours and, after being cooled, CH_2Cl_2 was extracted from the reaction mixture. The organic fractions were washed with water, dried over Na_2SO_4 and then filtered and evaporated under reduced pressure and then the crude product was purified by column chromatography over silica gel with a mixture of petroleum ether and EtOAc

(1:1, v:v) as eluent, resulted in the product N4,N4,N4′,N4′tetrakis-(4′-cynobiphenyl-4-yl)-biphenyl-4,4′-diamine (TPB-CN) as an orange solid with 85% yield (0.84 g). 1H NMR ($CDCl_3$, 500 MHz): 7.23 (m, 12H), 7.62 (m, 12H), 7.73 (m, 16H). Anal. Calcd for $C_{64}H_{40}N_6$: C, 86.07; H, 4.51; N, 9.41. Found: C, 86.49; H, 4.24; N, 9.26.

2.3. The Film of TPB-CN Compound

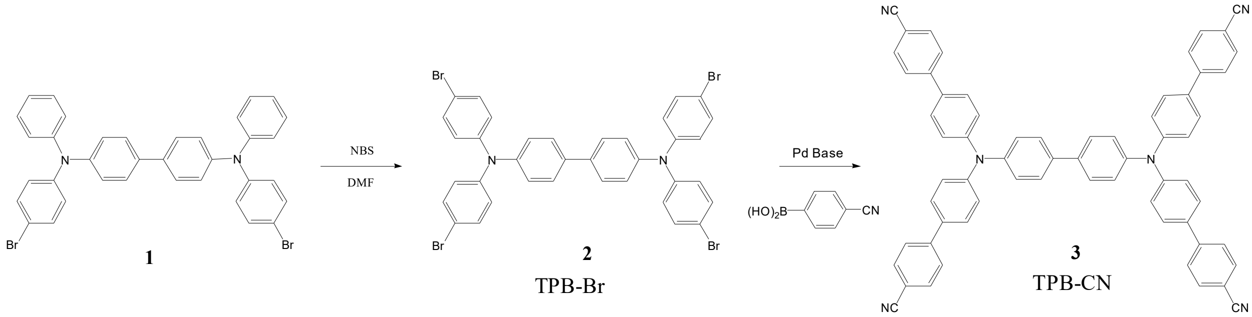
TPB-CN compound was dissolved in the chloroform solution. A film of TPB-CN compound was deposited by spin coating method at 1500 rpm for 30 s on glass substrate.

2.4. Quantum chemical calculations

Theoretical calculations were performed using density functional theory (DFT) to model the ground state molecular geometry, the energy gap and optical absorption spectra. For all calculations, the Gaussian09 program that includes DFT with the B3LYP functional and 6-31g(d,p) basis set was used [22]. The structure orientation has provided details for the electronic photophysical molecular properties of the compound TPB-CN. The ground state molecular geometry and the HOMO-LUMO energy gap of TPB-CN were calculated by DFT using the B3LYP functional, the 6-31g(d,p) basis set and MOPAC/PM6.

3. RESULTS AND DISCUSSION

Synthetic routes and chemical structures are shown in Scheme 1. As a result of an isolated form of the Pd(0)-catalyzed Suzuki-Miyaura cross coupling reaction, elemental analysis of the targeted TPB-CN compound which is usually soluble in most of organic solvents and defined by 1H and 13C NMR, was obtained as 85%.



Scheme 1. Synthetic route to the TPB-CN compound

Some optical properties of the designed molecule were identified by UV-vis absorption and fluorescence (FL). Figure 1(a) shows the absorption spectra of the TPB-CN compound in the 1 x10^{-5} mol/L dichloromethane solution and film. As seen in Fig. 1(a), two major bands appear in the absorption spectrum. The band between 350 and 400 nm can be referred to the transitions in four CN-phenyl groups, on the other hand the absorption band at between 240 and 300 nm can be attributed to n-π* transition of triphenylamine moiety. The compound exhibits blue emission with a maximum peak at 372 nm in solution and 380 nm in film, respectively, as a result, a blue-shift of 8 nm has been observed for the UV–Vis absorption peak of TPB-CN in dichloromethane. As shown in Table 1, Stokes' shift, belongs to thin film for the TPB-CN compound, is larger than the solution and these values are tabulated by 120 nm and 103 nm for thin film and polar solvent DCM, respectively. The absorption maxima of 433 nm in DCM was calculated by TD-B3LYP/6-31g(d,p). So, a difference, a little more than expected, has been observed between the experimentally obtained absorption wavelength maxima and the computed TD-B3LYP/6-31g(d,p). These values are tabulated in Table 1.

Table 1. Optical, thermal and theoretical properties of the TPB-CN compound

Compound	$\lambda_{abs}{}^{a}$ (nm)	$\lambda_{ems}{}^{b}$ (nm)	$\lambda_{calc}{}^{c}$ DCM/(nm)	$\Delta\lambda^{d}$ DCM/(nm)	$\Delta\lambda^{d}$ thin film/(nm)	Td/Tg (°C)
TPB(CN)$_4$	380(372)	483(492)	433	103	120	420/212

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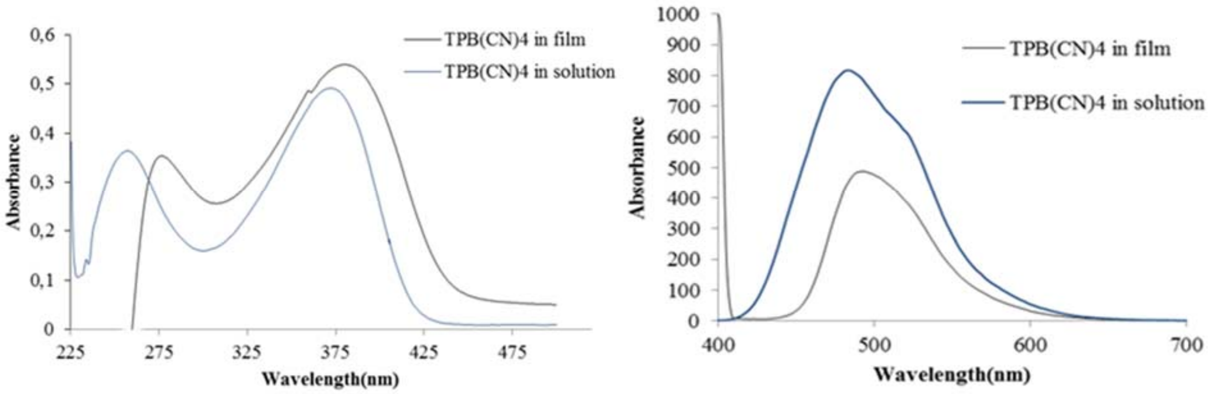
[a] Experimental absorption wavelength in 10^{-5} M solution of DCM. Values in parentheses correspond to absorption in thin film.

[b] Experimental emission wavelength in 10^{-5} M solution of DCM. Values in parentheses correspond to emission in thin film.

[c] Absorption wavelength using TD-B3LYP/6-31G(d,p) level in DCM.

[d] Stokes' shift $\Delta\lambda = \lambda ems - \lambda abs$

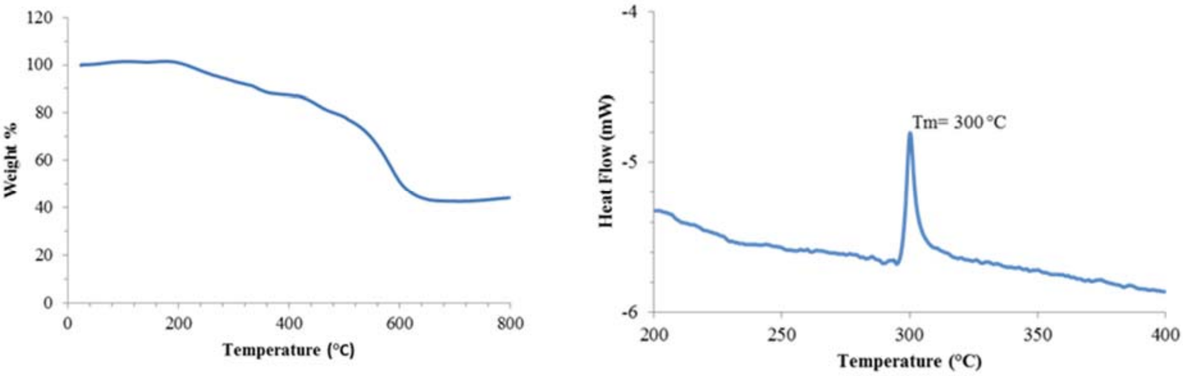
Figure 1b shows the fluorescence spectra of the TPB-CN compound. The fluorescence emission of TPB-CN reaches a peak of 483 nm in dichloromethane while that one in thin films was observed at 492 nm. As a result, there is a blue shift of 9 nm for the FL emission peak of TPB-CN in dichloromethane in the solvation effects. The observed blue shifts for both UV-absorption and FL spectra are almost the same.



(a) **(b)**

Figure 1. (a) UV–Vis absorption spectra of TPB-CN in solution (1 x10^{-5} mol/L) and in film; (b) FL spectra of TPB-CN in film and CH_2Cl_2 solution.

The thermal properties of TPB-CN were evaluated by TGA and DSC. TPB-CN is thermally stable up to 420 °C as shown in Figure (a) the TGA measurements. The onset temperature for 4.5% weight loss (T_d) of TPB-CN was 212 °C. DSC scan results of TPB-CN are shown in Figure 2b. In the first run of the DSC measurement, the sample melts at 300 °C (Tm), which gives an isotropic liquid sample.



(a) **(b)**

Figure 2. (a) TGA and; (b) DSC curves of TPB-CN

The XRD pattern of TPB-CN film carried out to estimate the crystallinity is illustrated in Figure 3. Observed strong diffraction peak approximately at 38.152° corresponds to the d-spacing between the molecular layers belonging to -CN groups in the TPB-CN, having about 2.356 Å distance. Another diffraction peaks were located at a 2θ of approximately 44.348°, 64.523°, 77.368° corresponding to a stacking distance of 2.040, 1.443, 1.232 Å respectively, which are due to stacking along the aryl groups in the TPB-CN molecule. These observed values imply that the molecular packing in the films is almost identical with those of single crystals.

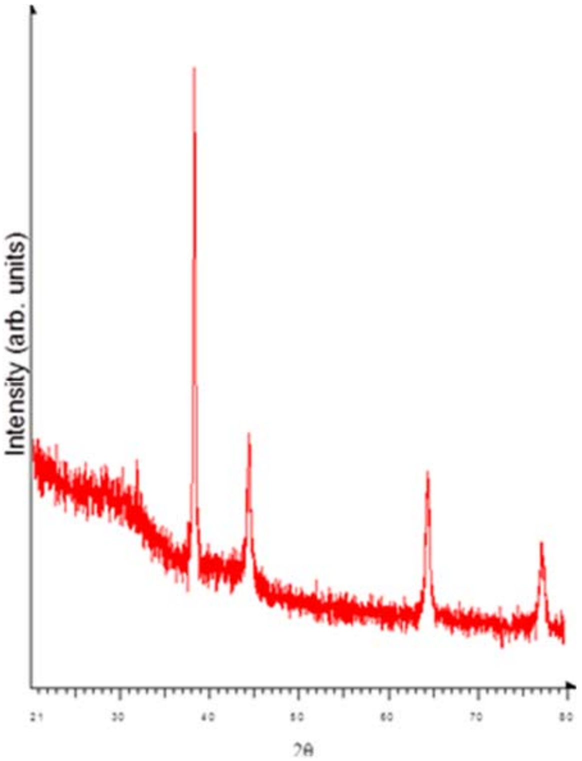
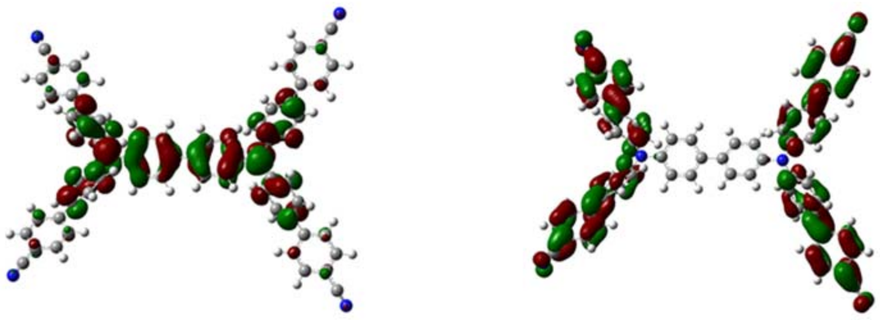


Figure 3. XRD pattern of the TPB-CN film

The distribution of HOMO and LUMO electron densities obtained by DFT calculation is shown in Figure 4. HOMO is mainly located on the TPB group, while LUMO is on –CN group.



(a) (b)

Figure 4. DFT calculations of (a) HOMO and (b) LUMO distribution for TPB-CN

The HOMO and LUMO levels, determined at B3LYP/6-31g(d,p) level and PM6, are shown in Table 2. The optical energy gaps of the TPB-CN compound were compared experimentally and theoretically. In this comparison, TPB-CN compound, the theoretically calculated one, is much lower than the other. Otherwise, the optical energy gap with a value of 7.304eV and calculated at PM6 is also very different from the others. The reason of the observed big differences between the optical and theoretical studies may be attributed to the fact that the results were obtained in different phases such as solvent, gas and film. Among them, the calculated one from onset of absorption in thin film form and the obtained value for TPB-CN film, are in good agreement with the literature reported for the properties between 2.0eV and 3.0eV [23]. Unfortunately, no correlation was observed between the experimental and the theoretical results.

Table 2. Electrothermal and theoretically properties of the compound

Compound	E_g^a (eV)	E_{HOMO}^b gas/(eV)	E_{LUMO}^b gas/(eV)	ΔE^c gas/(eV)	E_{HOMO}^b DCM/(eV)	E_{LUMO}^b DCM/(eV)	ΔE^c DCM/(eV)	E_{HOMO}^d PM6/(eV)	E_{LUMO}^d PM6/(eV)	ΔE^c PM6/(eV)
TPB-CN	2.93	-0.298	-0.219	0.079	-0.297	-0.218	0.079	-8.345	-1.041	7.304

[a] Calculated from onset of absorption in thin film,

[b] Calculated by DFT using the TD-B3LYP functional and the 6-31G(d,p) basis set,

[c] Calculated from optical energy gap $\Delta E = E_{LUMO} - E_{HOMO}$,

[d] Calculated by MOPAC using the PM6.

To have detailed information about the energy band gaps corresponding to the energy difference between HOMO and LUMO, the optical absorption measurements are carried out and the optical band gap may be estimated from the dependence of absorption coefficient on photon energy, using the following expression [24].

$$(\alpha h\nu) = \mathrm{B}\,(h\nu - E_g)^m$$

where, a is absorption coefficient, B is a constant and E_g is the optical band gap. In this expression, especially, m is a very crucial parameter because it characterizes how the optical absorption process occurs. If the exponent m is equal to 2 or ½, it means that indirect or direct performance of the optical absorption process allowed transitions. Figure 5 shows the plots of $(\alpha h\nu)^2$ vs. photon energy for the film, meaning that the process belongs to the direct allowed transitions. In the evaluation of this graph, the interception of $(\alpha h\nu)^2$ vs. hν curve gives the optical band gap value and it was found to be 2.93 eV.

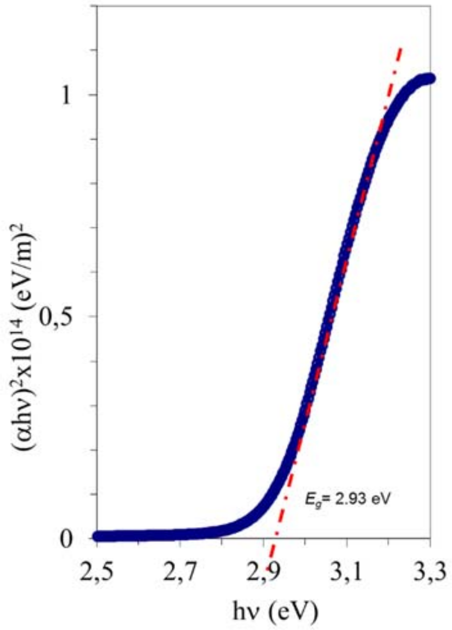


Figure 5. The plot of $(\alpha h\nu)^2$ vs. photon energy of the TPB-CN film

4. CONCLUSIONS

In this work, TPB-CN compound, which contains hole transporting components and can be soluble in most organic solvents, was designed, synthesized and identified by 1H NMR, 13C NMR and CHN elemental analysis. A little correlation was observed between the experimental and theoretical calculations performed to calculate absorption maxima in DCM by UV-Vis and TD-B3LYP/6-31g(d,p). TGA results show that TPB-CN compound can be used as a hole transporting molecular material in temperatures up to 420°C. After, TPB-CN compound was calculated theoretically for HOMO-LUMO levels by B3LYP/6-31g(d,p), the optical band gaps were determined to be found 0.079eV. The determined optical band gap value for the TPB-CN film was found to be 2.93 eV. Therefore, when both values are compared, theoretically calculated one is much lower than the other. Otherwise, the optical energy gap calculated at PM6 is also very different from the others with a value of 7.304eV. The reason of big differences observed between the optical and theoretical studies can be attributed to the fact that the results were obtained in different phases such as solvent, gas and film. Among these values, the obtained value for TPB-CN film is in good agreement with the literature which is reported between 2.0eV and 3.0eV. The XRD spectrum showed that TPB-CN compound might have a crystal structure.

ACKNOWLEDGEMENTS

I would like to thank Yasemin Çağlar, Müjgan Yaman and Halil Berber for the XRD, UV-vis measurements and theoretical calculation, respectively.

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