



# **FULL PAPER**

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Say hello wave goodbye: New electron-donor/acceptor-substituted tetraphenylethylenes exhibit aggregationinduced emission with tunable emission colors that range from blue to red. In addition, their microcrystals show 2D optical-waveguide behavior.



#### **Aggregation-Induced Emission**

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New Electron-Donor/Acceptor-Substituted Tetraphenylethylenes: Aggregation-Induced Emission with Tunable **Emission Color and Optical-Wave**guide Behavior

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### New Electron-Donor/Acceptor-Substituted Tetraphenylethylenes: Aggregation-Induced Emission with Tunable Emission Color and Optical-Waveguide Behavior

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Dedicated to Professor Chunli Bai on the occasion of his 60th birthday

Abstract: Herein, we report the synthesis of new tetraphenylethylene derivatives 1–5 that feature electron-donating (methoxy) and -accepting (dicyanomethane) groups as AIE-active molecules with tunable emission colors. The crystal structures of compounds 3 and 4 are described and the intermolecular interactions within their crystals agree with the observation that they exhibit strong solid-state emission. Compounds 1–4

### Introduction

Organic molecules that exhibit strong emission in the solid state have received increasing attention in recent years because of their promising applications in various areas, including OLEDs (organic light-emitting diodes) and relevant white-light-emitting devices.<sup>[1]</sup> Typically, organic fluorophores are emissive in solutions, but they become weakly fluorescent or non-fluorescent after aggregation or in the solid state.<sup>[2]</sup> However, Tang and co-workers discovered certain molecules that exhibited abnormal fluorescent behavior; they were weakly fluorescent (even non-fluorescent) in solution, but they lit up significantly after aggregation. Such unusual fluorescent phenomenon was referred to by the authors as aggregation-induced emission (AIE).  $^{\left[ 3\right] }$  Silole  $^{\left[ 4\right] }$  and tetraphenylethene (TPE)<sup>[5]</sup> are typical AIE molecules. These AIE molecules have been successfully utilized as solid-state emissive materials in OLEDs and in other devices.<sup>[6]</sup> More-

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exhibit typical AIE behavior and their emission maxima are red-shifted in the order: 1 < 2 < 3 < 4. Such red-shifts are ascribed to the fact that intramolecular interactions between the electron

**Keywords:** aggregation • electronic structure • emission • structure– activity relationships • tetraphenylethylenes

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donor and the electron acceptor become stronger with increasing number of methoxy groups. The solidstate emission colors of compounds **1–4** are successfully tuned from yellowgreen to red. Compound **5** shows AIE behavior, but its emission is only slightly enhanced after aggregation and its solid shows a low quantum yield. Furthermore, microplates of compound **3** exhibit 2D optical-waveguide behavior.

over, various chemo/biosensors are constructed by taking advantage of the AIE feature.<sup>[7,8]</sup> Accordingly, AIE molecules have been intensively explored over the past ten years and this emerging area has attracted more and more attention.<sup>[9]</sup>

Most of the reported AIE molecules emit within the wavelength range of blue and green light. For instance, silole and tetraphenylethylene molecules become strongly fluorescent after aggregation at about 480 nm.<sup>[4,5]</sup> Clearly, AIE molecules with tunable emission color are desirable. Tang and co-workers reported new AIE molecules with emissions in the long-wavelength region by conjugating TPE moieties at the periphery of normal fluorophores (e.g., perylene bisimide, pyrene, naphthalene, anthracene, and phenanthracene).<sup>[10]</sup> The authors also reported new AIE molecules by connecting two TPE moieties with conjugated groups, such as benzo-2,1,3-thiadiazole and thiophene.<sup>[11]</sup> Herein, we report an alternative strategy for developing new AIE molecules with tunable emission colors by connecting electrondonating and -accepting groups onto a TPE framework. The molecular design is based on the consideration that the incorporation of electron-donating (methoxy) and -accepting (dicyanovinyl) groups into a TPE framework will tune the HOMO/LUMO energies and, hence, the emission wavelengths can be tuned. The number of methoxy groups increases from compounds 1-5 (Scheme 1) and compounds 4 and 5 are different in the substitution pattern of the dicvanovinyl moiety. The results show that compounds 1-4, which feature methoxy and dicyanovinyl groups, show AIE behav-

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Scheme 1. Chemical structures of compounds 1–7.

ior with different emission colors that range from green to red. Moreover, crystals of compound **3** display 2D optical-waveguide behavior.

#### **Results and Discussion**

As an example, the synthesis of compound 1 is shown in Scheme 2. Compound 1-Br was obtained by a McMurry reaction in the presence of Zn and TiCl<sub>4</sub> in 31 % yield. Then, compound 1-Br was reacted with *n*BuLi and DMF to yield compound 1-CHO in 64 % yield. Compound 1 was obtained in almost-quantitative yield after the reaction of compound 1-CHO with dicyanomethane in the presence of Et<sub>3</sub>N. Compounds 2–5 were synthesized in a similar manner (for the synthetic details, see the Supporting Information). The chemical structures of compounds 1–5 were characterized by NMR spectroscopy and by MS (see the Experimental Section).

Single crystals of compounds 3 and 4 suitable for X-ray analysis were successfully obtained and their crystal struc-

#### **Abstract in Chinese:**

基于四苯乙烯骨架单元,在其上引入电子供体 (甲氧基)和电子受体(二氰基)衍生出一系列 发射调制可变的 AIE 类分子:化合物 1,2,3,4 和 5。通过 3 和 4 的晶体解析得出分子旋转受限 导致固态发射增强。从 1 到 4,随着电子供受体 的增加,固态发射从黄绿色逐渐红移到红色。5 也表现出 AIE 性质,但由于吸电子取代基位置的 变化,导致发光效率很低。另外,3 的微晶态表 现出很好的二维光波导性质.



Scheme 2. Synthetic route to compound 1. Reaction conditions: a) TiCl<sub>4</sub>, Zn in THF (31% yield); b) *n*BuLi, DMF, -78 °C (64% yield); c) CH<sub>2</sub>(CN)<sub>2</sub>, Et<sub>3</sub>N, RT (95% yield).

tures were determined. Disappointingly, efforts to grow good-quality crystals of compounds 1, 2, and 5 were unsuccessful. The molecular structures of compounds 3 and 4 are shown in Figure 1. Their bond lengths and angles are within the typical range. As anticipated, both compounds 3 and 4 adopt twisted conformations and the phenyl rings are not coplanar. For example, the C3-C4-C5-C6-C7-C8 phenyl



Figure 1. Molecular structures of compounds  ${\bf 3}$  and  ${\bf 4}$  depicted as thermal ellipsoids.

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ring in compound 3 forms a dihedral angle of 71.71° with the neighboring phenyl ring (C9-C10-C11-C12-C13-C14). Similarly, in compound 4, the C3-C4-C5-C6-C7-C8 phenyl ring is not coplanar with the neighboring phenyl ring (C17-C18-C19-C20-C21-C22), with a dihedral angle of 73.58°. In compound 3, the C12–C15 bond length (1.448 Å), which connects the dicyanomethane group to the TPE framework, is comparably shorter than that of the respective C27-C30 bond (1.462 Å) in compound 4; however, the C15–C16 bond (1.356 Å) in compound **3** is relatively longer than the respective C30-C31 bond (1.324 Å) in compound 4. Such a difference can be attributed to the intramolecular interactions between the electron-donor and -acceptor groups within compounds 3 and 4. The addition of one more methoxy group in compound 4 will enhance the electron-donating ability of the TPE framework and, accordingly, it is expected that the interactions between the electron-donor and -acceptor groups in compound 4 will be stronger than in compound 3.

The intermolecular orientation and arrangement within the crystals of compounds 3 and 4 are shown in the Supporting Information, Figures S1 and S2, respectively. Intermolecular  $\pi$ - $\pi$  interactions are not detected in either compounds 3 or 4; however, multiple short interatomic contacts exist within the crystals: O1…H (2.629, 2.505 Å), O2…H (2.502 Å), N1...H (2.621 Å), and N2...H (2.697 Å) interactions in compound **3** and O2…H (2.648 Å), O3…H (2.698, 2.645, 2.642 Å), N1---H (2.608, 2.701 Å), N2---H (2.658, 2.713 Å) interactions in compound 4. Furthermore, C–H $\cdots\pi$ interactions are detected in compound 3 (2.799, 2.797, and 2.645 Å) and compound 4 (2.840, 2.896, 2.761, 2.866, 2.839, 2.857, 2.648, 2.886, and 2.579 Å). These weak intermolecular interactions fix the molecular conformations of compounds 3 and 4 in the solid state, thus inhibiting the internal rotations and block their non-radiative relaxation, according to previous studies.<sup>[12]</sup> This result agrees well with the observation that both compounds 3 and 4 show strong emissions in the solid state, as discussed below.

Figure 2 shows the absorption spectra of compounds 1-4 in solution, as well as those of compounds 6 and 7 for comparison. Compounds 1-4 exhibit new, broad absorptions at around 394, 410, 425, and 440 nm, respectively, whereas compounds 6 and 7 absorb below 350 nm. Clearly, the absorption maximum is red-shifted in the order: 1 < 2 < 3 < 4. The appearance of such absorptions can be ascribed to intramolecular interactions between the electron-donor (methoxy) and -acceptor (dicyanomethane) groups in compounds 1-4; furthermore, the number of methoxy groups increases from compound 1 to compound 4 and, accordingly, the intramolecular electron-acceptor interactions gradually become stronger from compound 1 to compound 4. For example, DFT calculations were performed for compound 3. The HOMO is mainly localized on TPE and on the methoxy groups, but the dicyanomethane group also makes a slight contribution, as shown in Figure 3. Similarly, the LUMO is mainly localized on the dicyanomethane group, but the TPE fragment also contributes, albeit slightly. These calculation



Figure 2. Normalized absorption spectra of compounds 1, 2, 3, 4, 6, and 7 in THF; inset shows the absorption spectra of compound 5 in THF. The concentration of all compounds was  $2.5 \times 10^{-5}$  M.



Figure 3. HOMO and LUMO of compounds 3 and 5, based on the DFT calculations.

results clearly indicate the presence of intramolecular interaction between the electron-donor and -acceptor groups in compound 3.<sup>[13]</sup>

Compounds 3 and 5 are only different in terms of the substitution position of the dicyanomethane group, which is connected to TPE at the para and meta positions, respectively. However, their absorption spectra are completely different and compound 5 only shows absorption at around 320 nm, as shown in Figure 2, inset. Thus, the electronic structures of compounds 3 and 5 are largely affected by the substitution position of the dicyanomethane group. Indeed, this result is in agreement with the DFT calculations of compound 5. As shown in Figure 3, the HOMO is completely localized on the TPE and methoxy groups, whereas the LUMO completely resides on the dicyanomethane group. Therefore, the intramolecular interactions between the electron-donor and -acceptor groups in compound 5 should be rather weak. This result agrees with the difference between the absorption spectra of compounds 3 and 5 (Figure 2 and inset).

The fluorescence spectra of compounds **1–5** in solution were also recorded. As expected, these compounds are almost non-fluorescent in solution (Figure 4 and the Supporting Information, Figure S3), owing to internal rotations, according to previous studies.<sup>[2–5]</sup> However, the fluorescence of compounds **1–4** "turns on" upon aggregation. As an example, Figure 4 shows the fluorescence spectra of compound

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Figure 4. A) Fluorescence spectra of compound **3**  $(2.5 \times 10^{-5} \text{ M})$  in THF after the addition of various amounts of water (excitation wavelength: 430 nm). B) Plot of the relative fluorescence enhancement of compound **3** versus the volume fraction of water in THF/water mixtures; inset shows photographs of solutions of compound **3** in THF and THF/water (v/v, 5:95) under UV illumination (365 nm).

**3** in THF after the addition of different amounts of water. Clearly, the fluorescence intensity of compound **3** is significantly enhanced when the volume percentage of water is larger than 60%, as shown in Figure 4B. Such fluorescence enhancement can be detected by the naked eye, as shown in Figure 4B, inset, which shows photographs of compound **3** in THF and THF/water (5:95, v/v) under UV irradiation. As shown in the Supporting Information, Figure S2, the fluorescence intensities of solutions of compounds **1**, **2**, and **4** in THF also remarkably increase on the addition of water. Such fluorescence enhancement for compounds **1**–**4** is due to the formation of aggregates because these compounds are not water soluble<sup>[14]</sup> and, thus, the addition of water to their solutions in THF induces their aggregation, according to previous studies.<sup>[2-5]</sup> Therefore, compounds **1**–**4** 

show typical AIE behavior. Furthermore, compounds **1–4** show AIE emission maxima at 564, 603, 628, and 645 nm, respectively; thus, their emissions after aggregation are red-shifted with increasing number of methoxy groups. Accordingly, the emission colors of compounds **1–4** after aggregation can be successfully tuned, again owing to the fact that intramolecular interactions between the electrondonor and -acceptor groups become stronger with increasing number of methoxy groups in compounds **1–4**.<sup>[15]</sup> The emission properties of solid samples of compounds 1–4 that precipitated out from their respective solutions in THF after the addition of water were also examined. Table 1 summarizes the solid-state emission maxima of compounds 1–4, as well as their emission quantum yields and lifetimes. Their emission quantum yields are relatively high, reaching 0.61 for the solid sample of compound 2. They also show relatively long emission lifetimes in the nanosecond range. Clearly, the solid-state emissions of compounds 1–4 are red-shifted in the order: 1 < 2 < 3 < 4. Figure 5 shows fluorescence spectra and photographs of solid samples of compounds 1–4 under UV illumination. For comparison, the emission spectra of solids of compounds 6 and 7 are also in-



Figure 5. Normalized fluorescence spectra of (from left to right) compounds **1**, **2**, **3**, **4**, **6**, and **7** in the solid state; inset shows photographs of compounds **1**, **2**, **3**, **4**, **6**, and **7** under UV illumination (365 nm).

cluded in Figure 5. Clearly, the emission colors of compounds 6 and 7 and of compounds 1–4 vary from blue to green, yellow, orange, and even red. Thus, the emission colors of TPE compounds can be tuned by linking electrondonating (methoxy) and -accepting (dicyanomethane) groups.

The fluorescence spectra of compound 5 in THF after the addition of different amounts of water were also recorded. After aggregation, compound 5 shows an emission at around 595 nm, which is blue-shifted by 33 nm compared to that of compound 3 (see the Supporting Information, Figure S3). This shift is probably due to the fact the weak intra-molecular interactions between the electron-donor and -ac-

Table 1.	Photophysical	properties	of solid	compounds	1–5.
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Compound	Fl ( $\lambda_{max}$ ) [nm]	$arPsi_{ m f}^{[{ m a}]}$	$\tau_1 [\mathrm{ns}]/A_1 [\%]$	$\tau_2 [{\rm ns}]/A_2 [\%]$	$< \tau >^{[b]} [ns]$
1	564	0.54	0.508/58.2	3.223/41.8	1.643
2	603	0.61	0.564/45.8	3.011/54.2	1.890
3	628	0.52	0.575/43.1	2.646/56.9	1.753
4	645	0.48	0.459/46.5	4.195/53.5	2.458
5	595	0.03	2.058/31.9	9.851/68.1	7.365

[a]  $\Phi_i$  was measured by using a calibrated integrating sphere system. [b] An apparent decay time constant,  $\langle \tau \rangle$ , was determined by using the relationship  $\langle \tau \rangle = \Sigma(A_i \times \tau_i)/\Sigma A_i$  (i=1–n,  $n \approx 2$ –3), where  $\tau_i$  and  $a_i$  represent the individual exponential decay-time constant and the corresponding pre-exponential factor, respectively.<sup>[16]</sup> Fl=fluorescence.

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ceptor groups in compound 5, as discussed above. As shown in the Supporting Information, Figure S3, the fluorescence of compound 5 is also enhanced after aggregation in THF/ water (5:95, v/v). However, the aggregation-induced fluorescence enhancement for compound 5 is remarkably small compared to that for compound 3 under the same conditions. As listed in Table 1, the emission quantum yield of a solid sample of compound 5 is 0.03, much lower than that of compound **3** ( $\Phi = 0.52$ ). One possible explanation for this result is that the intermolecular packing within the aggregates of compound 5 is loose<sup>[17]</sup> and, as a result, the internal rotations are only inhibited for a limited number of molecules within the aggregates, thus leading to a slight fluorescence enhancement. However, the emitted molecules within the solid sample of compound 5 exhibit a relatively long emission lifetime (Table 1).

Microplates of compound 3 (quasi-rectangular shape) were successfully obtained by crystallization. Near-field scanning optical microscopy (NSOM) was used to investigate the solid-state emission behavior of microplates of compound 3. Figure 6A shows the photoluminescence (PL) of microplates of compound 3 under UV illumination (330-380 nm). Clearly, bright, red-light emissions were detected from the four edges, whilst those from the body of microplates were remarkably weak. Such solid-state emission behavior is characteristic for optical waveguides.<sup>[18]</sup> As shown in Figure 6B, red-light emissions were detected at six spots around the edges of the microplate of compound 3 after excitation in its center with a focused laser (351 nm). In general, the emission light can only be observed at the local area of the excited position. The appearance of the out-coupling light at the edges of the microplates of compound 3 is a typical characteristic of 2D waveguide behavior. Because the waveguided light is generated from the PL, microplates of compound 3 can be classified as active 2D waveguides, based on previous reports.[19]

The corresponding emission spectra at the six spots and in the center were collected (Figure 6 C). Compared to that at the center, the emission spectra at the six spots are both red-shifted and weakened. Because there is overlap between the corresponding absorption and fluorescence spectra of compound **3** in the solid state (see the Supporting Information, Figure S4), self-absorption may be responsible for the observed red-shifts and optical loss. In addition, the optical loss can be also induced by: 1) the effect of the glass substrate and 2) Rayleigh scattering, owing to defects within the microplates, which will lead to local variation of the refractive index within the microplates.<sup>[18,19]</sup>

Alternatively, guided red-light emissions were only detected at the two ends of the edge of the microplate of compound **3** at which the excitation laser was focused (see the Supporting Information, Figure S5). When the excitation laser was focused on one of the four corners of the microplate of compound **3**, the guided red-light emission mainly appeared at the respective end of the edge (see the Supporting Information, Figure S5). The emission spectra at the respective ends of the edges were recorded; similarly, the



Figure 6. A) Photoluminescence (PL) image of the microplates of compound **3**. B) Micro-area PL image that was obtained by exciting the center of the microplate of compound **3**. C) Corresponding spatially resolved PL spectra at the excitation position (A0) and of the out-coupled light (A1–A6).

guided emissions were red-shifted and weakened compared to the respective emissions at the excited spots (see the Supporting Information, Figure S5).

#### Conclusions

New tetraphenylethylene derivatives **1–5**, which feature electron-donating (methoxy) and -accepting (dicyanomethane) groups, have been designed and investigated as AIE-active molecules with tunable emission colors. Absorption spectroscopic analysis revealed that intramolecular electron-donor/acceptor interactions existed within compounds **1–4**. Crystal structures of compounds **3** and **4** were also deter-

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mined. Compounds 1-4 exhibited typical AIE behavior and their emission maxima were red-shifted in the order: 1 < 2 <3 < 4. Such red-shifts are due to the fact that intramolecular interactions between the electron-donor and electron-acceptor groups become stronger on increasing the number of methoxy groups in compounds 1-4. The solid-state emission of compounds 1-4 was also investigated; these compounds exhibited high emission quantum yields and their emission colors varied from yellow to red. Interestingly, alteration of the substitution pattern of the dicyanomethane group from para (in 3) to meta (in 5) significantly affected the emissive feature of compound 5. Compound 5 showed AIE behavior, but its emission was only slightly enhanced after aggregation and its solid showed a low quantum yield. Furthermore, microplates of compound 3 exhibited 2D optical-waveguide behavior. These results indicate that the connection of electron-donating and -accepting groups onto the TPE framework is a useful strategy for inventing new AIE-active molecules with tunable emission colors. Further functionalization of these new AIE molecules (in particular for compound 4 with red AIE) is underway for applications in biosensing and bioimaging.

#### **Experimental Section**

#### General

All chemicals were purchased from Alfa Aesar and used without further purification. Water was purified by using a Millipore filtration system. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. MS (MALDI-TOF) were recorded on a BEFLEX III spectrometer. Absorption spectra were recorded on a JASCO V-570 UV/Vis spectrophotometer. Steady-state fluorescence spectra were recorded on Hitachi (F-4500) spectrophotometers at 25 °C. All photographs were taken with a Canon digital camera. Density functional theory (DFT) calculations were performed at the B3LYP/6-31G\* level of theory by using the Gaussian 09 program package (revision A.02).[20]

#### Crystal-Structure Analysis

Crystals of compounds 3 and 4 were grown by the slow evaporation of their solutions in CH2Cl2/petroleum ether. All diffraction data were collected on a Rigaku Saturn diffractometer with a CCD area detector. All calculations were performed by using SHELXL97 and the crystallographic software packages. CCDC 889341 (3) and CCDC 889342 (4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

#### Photophysical Studies

Quantum efficiencies of compounds 1-5 in the solid state were determined on a FLSP 920 fluorescence spectrometer with a calibrated integrating sphere system. Fluorescence lifetimes of compounds 1-5 were measured, based on time-resolved PL experiments with a regenerative amplified Ti:sapphire laser (Spectra-Physics, Spitfire) at 400 nm (pulse width: 150 fs, second harmonic). The PL spectra were recorded by using a streak camera (C5680, Hamamatsu Photonics) that was attached to a polychromator (Chromex, Hamamatsu Photonics), for which the temporal and spectroscopic resolutions of the detector were about 10 ps and 2 nm, respectively. All of the spectroscopic measurements were performed at RT.

**Optical-Waveguide Behavior** 

To measure the micro-area PL spectra of microplates of compound 3, a dispersion of the microplates over a glass cover-slip was excited with a UV laser ( $\lambda = 351 \text{ nm}$ , Beamlok, Spectra-Physics). The excitation laser was filtered with a band-pass filter (330-380 nm) and then focused to excite the microplates with an objective lens (×50, N.A. = 0.80; N.A., numerical aperture).

#### Typical Synthesis of Compound 1

Both compounds 1-Br and 1-CHO were synthesized according to literature procedures.<sup>[21]</sup> 1-CHO (360 mg, 1.0 mmol) and CH<sub>2</sub>(CN)<sub>2</sub> (99.8 mg, 1.5 mmol) were dissolved in dry CH2Cl2 (10 mL) and one drop of Et3N was added to the solution. The mixture was stirred for about 2 h at RT. Then, the mixture was washed with water  $(3 \times 50 \text{ mL})$  and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvents, the residue was purified by column chromatography on silica gel to afford compound 1 (387.5 mg). Compounds 2-5 were synthesized in a similar manner.

**Compound 1**: Yield: 95 %; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.65$  (d, 2H), 7.61 (s, 1H), 7.22–7.08 (m, 11H), 7.07–6.94 ppm (m, 6H); <sup>13</sup>C NMR  $(100 \text{ MHz}, \text{ CDCl}_3): \delta = 159.1, 151.1, 144.0, 142.7, 142.6, 142.5, 139.2,$ 132.4, 131.2, 131.1, 130.2, 128.8, 128.0, 127.7, 127.3, 127.0, 114.0, 112.8, 81.2 ppm; HRMS (EI): m/z calcd for  $C_{30}H_{20}N_2$ : 408.1626; found: 408.1632; elemental analysis calcd (%) for C<sub>30</sub>H<sub>20</sub>N<sub>2</sub>•0.1 CH<sub>2</sub>Cl<sub>2</sub>: C 86.70, H 4.88, N 6.72; found: C 86.73, H 4.95, N 6.83.

**Compound 2**: Yield: 95 %; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.66$  (d, 1 H), 7.64-7.58 (m, 2H), 7.16 (t, 8H), 7.03 (d, 4H), 6.92 (d, 2H), 6.65 (t, 2H), 3.77–3.74 ppm (d, 3H);  ${}^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ =159.1, 158.6, 151.6, 151.5, 143.7, 143.0, 142.9, 138.3, 138.2, 135.1, 132.6, 132.5, 132.4, 131.3, 130.3, 130.2, 128.6, 128.1, 128.0, 127.6, 127.3, 126.8, 114.0, 113.4, 113.1, 112.8, 81.0, 55.1, 55.0 ppm; HRMS (EI): *m/z* calcd for C<sub>31</sub>H<sub>22</sub>N<sub>2</sub>O: 438.1732; found: 438.1738; elemental analysis calcd (%) for  $C_{31}H_{22}N_2O{\boldsymbol{\cdot}}0.1\,CH_2Cl_2;\ C\,83.56,\ H\,5.01,\ N\,6.27;\ found:\ C\,83.30,\ H\,5.00,$ N 6.23.

**Compound 3**: Yield: 95 %; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.64$  (d, 2H), 7.60 (s, 1H), 7.15 (d, 5H), 6.99 (d, 2H), 6.96-6.84 (m, 4H), 6.65 (dd, 4H), 3.77 (s, 3H), 3.74 ppm (s, 3H);  ${}^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 159.0$ , 158.8, 158.5, 152.0, 143.5, 143.1, 137.4, 135.3, 135.2, 132.7, 132.6, 132.4,  $131.3,\ 130.3,\ 128.4,\ 128.0,\ 126.7,\ 114.1,\ 113.4,\ 113.0,\ 112.9,\ 80.7,\ 55.1,$ 55.0 ppm; HRMS (EI): *m/z* calcd for C<sub>32</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>: 468.1838; found: 468.1845; elemental analysis calcd (%) for  $C_{32}H_{24}N_2O_2 \cdot 0.05 CH_2Cl_2$ : C 81.42, H 5.14, N 5.93; found: C 81.27, H 5.12, N 6.02.

**Compound 4**: Yield: 95 %; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.64$  (d, 2H), 7.60 (s, 1H), 7.16 (d, 2H), 6.92 (dd, 6H), 6.67 (d, 6H), 3.76 ppm (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 159.1$ , 158.7, 158.4, 158.2, 152.3, 142.6,  $137.1,\ 135.6,\ 135.5,\ 132.7,\ 132.5,\ 132.4,\ 130.3,\ 128.4,\ 114.2,\ 113.4,\ 113.3,$ 113.1, 112.9, 80.5, 55.1 ppm; HRMS (EI): m/z calcd for C<sub>33</sub>H<sub>26</sub>N<sub>2</sub>O<sub>3</sub>: m/z 498.1943; found: 498.1949.

**Compound 5**: Yield: 95 %; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.77$  (d, 1 H), 7.53 (s, 1H), 7.39 (s, 1H), 7.28 (s, 2H), 7.13 (s, 3H), 7.00 (d, 2H), 6.93 (d, 4H), 6.65 (t, 4H), 3.76 (s, 3H), 3.74 ppm (s, 3H);  $^{13}\mathrm{C}\,\mathrm{NMR}$  (100 MHz,  $CDCl_3$ ):  $\delta = 159.9$ , 158.4, 158.3, 146.1, 143.1, 142.1, 137.6, 136.8, 135.3, 135.2, 134.6, 132.6, 132.4, 131.2, 130.5, 129.0, 128.0, 127.2, 126.6, 113.7, 113.3, 113.0, 112.4, 82.2, 55.1, 55.0 ppm; HRMS (EI): m/z calcd for C32H24N2O2: 468.1838; found: 468.1843; elemental analysis calcd (%) for C32H24N2O2: C 82.03, H 5.16, N 5.98; found: C 81.95, H 5.40, N 5.90.

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