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Graphical Abstract

Novel 2-substituted-4,5-diphenyl-1*H*-imidazoles (**M1-M4**) have been synthesized via the solvent-free Debus-Radziszewski reaction. They emit up-converted fluorescence, and the two-photon absorption cross-sections are 585, 31, 34, and 1193 GM in DMF, respectively.



Synthesis and two-photon absorption properties of novel 2-substituted-4,5-diphenyl-1*H*-imidazoles

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Abstract

Novel 2-substituted-4,5-diphenyl-1*H*-imidazoles (**M1-M4**) were synthesized via a three-component, one-pot reaction under solvent-free conditions. The structures were characterized by infrared, hydrogen-1 nuclear magnetic resonance, carbon-13 nuclear magnetic resonance, mass spectrometry and elemental analysis. Their UV-visible absorption, single-photon excited fluorescence, two-photon absorption, and two-photon excited fluorescence were systematically investigated in different solvents. Pumped by femtosecond laser pulses, **M1** and **M4** exhibit large two-photon absorption cross-sections (585 and 1193 GM in DMF, respectively). The quantum chemical density functional theory calculations offer complementary information regarding the frontier orbitals and the molecular structures, which confirm that the degree of intramolecular charge transfer plays an important role in enhancing two-photon absorption properties.

Keywords: Two-photon absorption; Solvent-free; Imidazole; Synthesis

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1. Introduction

In recent years, a tremendous amount of interest has been attracted to materials with two-photon absorption (TPA) properties for their potential applications, such as two-photon dynamic therapy,¹⁻³ up-converted lasing,⁴ optical power limiting,⁵⁻⁷ three-dimensional data storage,⁸⁻⁹ three-dimensional microfabrication,¹⁰⁻¹² and fluorescent probes in living cell imaging studies.¹³⁻¹⁵ So far, much effort has been devoted to designing and synthesizing TPA materials with large TPA cross-sections (σ) as well as high fluorescence quantum yields (Φ).¹⁶⁻¹⁸

Among the reported TPA systems, the heterocycle-based chromphores represent a growing class of TPA materials, and have evoked special attention.¹⁹⁻²² Imidazole, the N-heterocycle molecule, has high electron-withdrawing ability, good coplanarity, and good thermal stability, which render it to be an ideal building block for nonlinear optical materials.²³⁻²⁵ In addition, imidazole derivatives have been shown to exhibit interesting biological activities, including anti-allergy,²⁶ anti-tumor,²⁷ anti-inflammatory,²⁸ anti-bacterial,²⁹ and analgesic.³⁰ Hence, imidazole plays an important role in biochemistry, medical science, nonlinear optical materials and so on.

Organic solvents occupy a very large part on the list of damaging chemicals. In recent years, solvent-free organic reactions have caused great interest. Debus-Radziszewski³¹ reaction is a commonly used method to synthesize imidazoles, most of which were prepared using solvents. So the development of synthetic methods enabling environment-friendly access to this heterocycle is still desirable. 2-Substituted-4,5-diphenyl-1*H*-imidazoles are generally synthesized by three-component cyclocondensation of benzil with an aldehyde and ammonium acetate, which comprises the use of refluxing in AcOH.³² Obviously, this method usually produces a large amount of waste acid that limits its utility.

In this paper, a simple, mild, environmentally benign, and efficient method has been used for the preparation of four new 2-substituted-4,5-diphenyl-1*H*-imidazole derivatives

M1-M4 (scheme 1) starting from benzil, ammonium acetate and various aromatic aldehydes under solvent-free conditions.³³ The target imidazole derivatives are in the form of A- π -A (**M1**), A- π -D (**M2**), A-D-A (**M3**), and A- π -D- π -A (**M4**), respectively. (D: electron donating group, A: electron accepting group, π : conjugated pathway). Their linear and nonlinear optical properties have been systematically investigated in different solvents. Meanwhile, the quantum chemical calculations have been performed to provide deep insight into the electronic structures and the optical properties of these imidazole derivatives. Detailed results and discussion are presented in the following sections.

2. Results and discussion

2.1. Synthesis and characterization

The detailed synthetic routes of four imidazole derivatives M1-M4 are described in Scheme 2. 4-[(1E)-2-(4-Formylphenyl)ethenyl]benzonitrile (3a) was achieved following a one-pot two-step reaction, involving the Horner-Wadsworth-Emmons (HWE) reaction between 4-(diethoxymethyl)benzaldehyde (1a) and [(4-cyanophenyl)methyl]phosphonic acid diethyl ester (2a) with high trans-stereoselectivity and subsequent hydrolysis under mild acidic conditions with aqueous acetic acid. Using potassium tert-butoxide as catalyst and DMF as solvent, 4-(9H-carbazol-9-yl)benzaldehyde (1b) was prepared by direct reaction of 9H-carbazole with 4-fluorobenzaldehyde. 9-ethyl-9H-Carbazole-3,6dicarboxaldehyde (1c) was obtained by the Vilsmeier formylation reaction of 9-ethyl-9H-carbazole with DMF POCl₃. 1,4-Bis(bromomethyl)-2,5and dimethoxybenzene (1d) was prepared via the Blanc reaction of 1,4-dimethoxybenzene (HCHO)_n with and HBr, then reacted with P(OEt)₃ vield to [(2,5-dimethoxy-1,4-phenylene)bis(methylene)]bisphosphonic acid tetraethyl ester (2d). 4,4'-[(2,5-Dimethoxy-1,4-phenylene)di-(1E)-2,1-ethenediyl] bisbenzaldehyde (3d) was synthesized by the similar experimental conditions described for 3a. M1-M4 were prepared from benzil, the corresponding aromatic aldehydes (3a, 1b, 1c, and 3d), and ammonium acetate under solvent-free conditions as shown in Scheme 2. It is noteworthy that the target compounds are easily collected and purified.

The FT-IR spectra of **M1-M4** exhibit absorption frequencies at 3398-3420 cm⁻¹ for NH group of the imidazole ring. The ¹H NMR spectra of **M1-M4** exhibit one singlet at 12.66-12.90 ppm due to the NH group of the imidazole ring. For **M1** and **M4**, the (*E*)-configurations of the C-C double bonds are certified by the coupling constants ³J (H, H) = 16.5 Hz for the olefinic AB spin systems. In addition, it is striking to note a signal at m/z 316.8 for **M3** and 390.5 for **M4**, this can be interpreted as doubly protonated molecular ion ([M+2H]²⁺) of **M3** and **M4**.





Scheme 1. Molecular structures of M1-M4.





Scheme 2. Synthesis of M1-M4.

2.2 Linear absorption and single-photon excited fluorescence

The linear photophysical data of **M1-M4** in various solvents with different polarity are listed in Table 1. The corresponding linear absorption spectra and single-photon excited fluorescence (SPEF) spectra are displayed in Fig. 1 and Fig. 2.

Compound	Solvent	λ_{\max}^{abs}	$10^{-4} \varepsilon^{b}$	$\lambda_{\max}^{\text{SPEF}^{c}}$	$\Delta \nu^{d}$	$arPhi^{ m e}$
	2011011	(nm)	$(\mathrm{mol}^{-1} \mathrm{L} \mathrm{cm}^{-1})$	(nm)	(cm ⁻¹)	6
M1	THF	378	7.65	486	5879	0.49
	CH_2Cl_2	374	8.46	492	6413	0.35
	DMF	378	3.60	517	7113	0.28
	CH ₃ CN	373	6.92	519	7542	0.21
M2	THF	331	3.69	391	4636	0.51
	CH_2Cl_2	331	9.09	396	4959	0.55
	DMF	331	10.28	398	5086	0.52
	CH ₃ CN	329	6.63	400	5396	0.61
M3	THF	312	2.85	413	7838	0.43
	CH_2Cl_2	310	8.08	416	8220	0.48
	DMF	311	14.75	418	8231	0.38
	CH ₃ CN	307	8.63	421	8820	0.46
M4	THF	426	8.93	478	2554	0.72
	CH ₂ Cl ₂	428	8.09	481	2574	0.64
	DMF	429	15.69	483	2606	0.51
	CH ₃ CN	424	1.77	487	3051	0.32

Table 1. Linear absorption and single-photon excited fluorescence properties of M1-M4.

^a Maximum linear absorption wavelength, $c = 1 \times 10^{-5} \text{ mol } L^{-1}$.

^b Maximum molar absorption coefficient.

^c Maximum single-photon excited fluorescence wavelength, $c = 1 \times 10^{-6} \text{ mol } L^{-1}$.

^d Stokes shift.

^e Fluorescence quantum yield, measured by using quinine sulfate in 0.5 mol L⁻¹ sulfuric acid (**M1-M3**) and fluorescein in 0.1 mol L⁻¹ sodium hydroxide (**M4**) as the standards.





Fig. 1. Linear absorption spectra of M1-M4 in various solvents with a concentration of 1×10^{-5} mol L⁻¹.





Fig. 2. Single-photon excited fluorescence spectra of **M1-M4** in various solvents with a concentration of 1×10^{-6} mol L⁻¹.

As shown in Fig. 1, two absorption peaks can be observed, the one in the shorter wavelength region is attributed to the π - π * transition arising from the phenyl rings attached at positions 4 and 5 of the imidazole ring, and that in the longer wavelength region can be classed into two types: M1 and M4 show the absorption peaks around λ_{max}^{abs} = 375 and 426 nm, respectively, which are accredited to intramolecular charge transfer (ICT) character. Moreover, the second bands of M2 and M3 in the UV region (around 330 and 310 nm, respectively) are characteristic of carbazole π - π * transition. There is only slight shift (± 5 nm) for the absorption spectra of **M1-M4** upon changing the solvents from THF to CH₃CN, indicating that the polarity of solvents has little effect on the absorption transition. Compared with M2 and M3, a prominent red-shift in absorption spectra of M1 and M4 is attributed to the longer π -conjugated chain by introducing a styrene π -bridge. In highly polar DMF, M2-M4 possessing one or two donors display the strongest light absorption capacity, whose molar absorption coefficients (ε) are 10.28×10⁴, 14.75×10⁴, and 15.69×10⁴ mol⁻¹ L cm⁻¹, respectively. While M1 without any donor manifests the poorest absorption capacity in DMF (ε = $3.60 \times 10^4 \text{ mol}^{-1} \text{ L cm}^{-1}$).

The SPEF spectra of **M1-M4** in different solvents were obtained under the excitation at their maximum absorption wavelengths. It is noticeable that the effect of solvent polarity on the emission behavior is more pronounced than that on the absorption behavior. As shown in Fig. 2, all the target compounds are sensitive to four different solvents ranging from THF to CH₃CN: the higher polarity the solvent has, the greater red-shift the compounds display. The Stokes shift (Δv) of each compound shows the same tendency with the $\lambda _{max}^{SPEF}$ as the polarity of solvents increases. These observations suggest that the excited state of the compounds is more polar than the ground state. In THF and CH₂Cl₂ with medium polarity, **M4** exhibits dual emission behavior. The emission peak around 479 nm is assigned to the locally excited (LE) state and the longer emission wavelength centered around 510 nm is assigned to the ICT state. In DMF and CH₃CN with high

polarity, the emission peak of M4 around 510 nm degenerates into a shoulder, which can be explained by the intense ICT between the electron donor and the electron acceptor resulting from the strong solute-solvent interaction. Different from the absorption properties, the $\lambda_{\text{max}}^{\text{SPEF}}$ of M1-M4 can be sequenced as M1 > M4 > M3 > M2, which implies that the molecular polarity in the excited state changes in the same order.

The fluorescence photos of **M1-M4** in DMF are displayed in Fig. 3, from which one can clearly see that under the irradiation of UV light at 365 nm, **M1** and **M4** emit green (517 nm) and cyan (483 nm) fluorescence, respectively. While **M2** and **M3** emit violet (398 nm) and blue (418 nm) fluorescence, respectively.

IVI I IVIZ IVIS IVI4	M1	M2	M3	M4
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Fig. 3. Fluorescence photos of M1-M4 in DMF.

The fluorescence quantum yield (Φ) was determined by using quinine sulfate in 0.5 mol L⁻¹ sulfuric acid ($\Phi = 0.546$)³⁴ (**M1-M3**) and fluorescein in 0.1 mol L⁻¹ sodium hydroxide ($\Phi = 0.9$)³⁴ (**M4**) as the standards. The Φ was obtained as follows:

$$\Phi_{\rm s} = \Phi_{\rm r} \frac{n_{\rm s}^2}{n_{\rm r}^2} \frac{F_{\rm s}}{F_{\rm r}} \frac{A_{\rm r}}{A_{\rm s}}$$

where the s and r subscripts designate the sample and the reference, respectively. A is the absorbance at the excitation wavelength, n is the refractive index of the relevant solution, and F is the integrated area under the corrected emission spectrum.

As shown in Table 1, the Φ of M2 and M3 are slightly susceptible to solvent polarity. While one can see that the Φ of M1 and M4 decrease consistently and significantly as the polarity of solvents increases. This fluorescent behavior can be ascribed to "twisted intramolecular charge transfer (TICT)" upon the excited state.³⁵ TICT is a process of intramolecular transfer from the donor to the acceptor on the excited state accompanied by the twisted structure geometry. It is much less emissive and strongly dependent on the polarity of solvents. An increase in the polarity of solvents can decrease the activation barrier and enhance the TICT process.

2.3 Two-photon absorption properties

Taking advantage of the fluorescent properties of **M1-M4**, their TPA properties in the near infrared (NIR) range (680-1000 nm) could be determined by using the two-photon induced fluorescence technique with femtosecond laser pulses. The nonlinear photophysical properties of **M1-M4** in THF and DMF were recorded under 500 mW from 680 nm to 930 nm, and the corresponding data are listed in Table 2 and shown in Fig. 4.







Fig. 4. Two-photon absorption cross-sections of **M1-M4** in THF (a) and DMF (b) in the 680-930 nm region.

Table 2

Two-photon absorption and two-photon excited fluorescence properties of M1-M4.

Compound	Solvent	$\lambda \frac{\text{TPEF a}}{\max}$	$\sigma_{ m max}{}^{ m b}$
compound (Solvent	(nm)	(GM)
M1	THF	525	373
	DMF	561	585
M2	THF	431	25
	DMF	445	31
M3	THF	458	28
	DMF	471	34

M4	THF	530	733
	DMF	535	1193

^a Maximum two-photon excited fluorescence wavelength, $c = 1 \times 10^{-3} \text{ mol } \text{L}^{-1}$.

^b Two-photon absorption cross-section, $1 \text{ GM} = 1 \times 10^{-50} \text{ cm}^4 \text{ s photon}^{-1}$.

The σ value was obtained by comparing the two-photon excited fluorescence (TPEF) intensity of the sample with that of a reference compound by the following equation.

$$\boldsymbol{\sigma}_{\mathrm{s}} = \frac{F_{\mathrm{s}}}{F_{\mathrm{r}}} \frac{\boldsymbol{\Phi}_{\mathrm{r}}}{\boldsymbol{\Phi}_{\mathrm{s}}} \frac{\boldsymbol{n}_{\mathrm{r}}}{\boldsymbol{n}_{\mathrm{s}}} \frac{\boldsymbol{c}_{\mathrm{r}}}{\boldsymbol{c}_{\mathrm{s}}} \boldsymbol{\sigma}_{\mathrm{r}}$$

where the subscripts s and r denote the sample and the reference. *F* and Φ represent the TPEF integral intensity and the fluorescence quantum yield. *n* and *c* are the refractive index and the concentration of the solution. In this work, we selected fluorescein in 0.1 mol L⁻¹ sodium hydroxide (c = 1×10⁻³mol L⁻¹) as the reference (σ = 36 GM³⁶).

As observed from Fig. 4, the excitation wavelengths of M1-M4 at maximum σ values in THF and DMF are both at 750 nm, 680 nm, 680 nm, and 850 nm, respectively. The corresponding maximum σ values are 585 GM for M1, 31 GM for M2, 34 GM for M3, and 1193 GM for M4 in DMF with the sequence of M4 > M1>>M3 > M2, which is better than those in THF.

In an effort to understand the relationship between the σ of M1-M4 and the distribution of electron densities over the molecules and hence the electronic properties, the density functional theory (DFT) calculations were performed and the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the M1-M4 were analyzed. The calculation results are shown in Fig. 5.



Fig. 5. Optimized geometrical structures, HOMO and LUMO distributions of M1-M4.

Clearly, the σ values of M2 and M3 are much smaller than those of M1 and M4, probably because our wavelengths of light source range from 680 nm to 1080 nm. This range cannot meet their relative twofold λ_{max}^{abs} . On the other hand, M2 and M3 have

non-planar geometries that interfere with electron transfer across the molecule, the more largely the electron transfer is impeded, the smaller σ the molecule should have. For **M1**, Fig. 5 shows that the electron clouds of the HOMO are mainly localized on the styrene π -bridge, the imidazole unit, and the C-5 benzene ring. However, it is notable that the electron clouds of the LUMO are spread over the styrene π -bridge and the electron-poor benzonitrile due to the strong electron-withdrawing ability of the cyano group. The result indicates that there is a good charge-separated state between the HOMO and the LUMO of **M1**, which leads to the relatively large σ value. Though the HOMO-LUMO transitions of **M1** and **M4** both bear ICT nature besides the π - π * transition, the σ value of **M4** is about 2 times as large as that of **M1**, suggesting that the longer conjugation length, the pseudo-one-dimensional geometry, and the bidirectional charge transfer obviously improve the TPA ability. The σ value shows negative correlation with energy gap between the HOMO and the LUMO. The corresponding energy gaps of **M1-M4** were calculated to be 0.115, 0.145, 0.142, and 0.103 eV, respectively, which is in agreement with the sequence of σ (**M4** > **M1**>>**M2**).

It can be seen from Table 2 that the fluorescence peak wavelengths of TPEF are evidently red-shifted by 39-52 nm compared with those of SPEF in THF and DMF, which can be explained by the reabsorption effect.

The representative TPEF spectra of **M4** in DMF pumped by femtosecond laser pulses at 500 mW under different excitation wavelengths are presented in Fig. 6. One can see that **M4** exhibits various TPEF intensity under different excitation wavelengths. For **M1**, the optimal excitation wavelength is 850 nm. Fig. 7a and 7b show the TPEF intensities of **M4** under different pump powers and the logarithmic plot of the output fluorescence integral versus the input powers. The logarithmic plot has a slope of 2.01 when the input laser power is increased. It provides the direct evidence for the squared dependence of the fluorescence intensity and the input power, suggesting a two-photon excitation mechanism. As the nonlinear absorption is observed in the range from 680 nm to 930 nm,



so the emission can also be attributed to the TPEF mechanism. The other compounds (**M1-M3**) are also proved to have the same excitation mechanism.

Fig. 6. Two-photon excited fluorescence spectra of **M4** in DMF ($c = 1 \times 10^{-3} \text{ mol } \text{L}^{-1}$) pumped by femtosecond laser pulses at 500 mW under different excitation wavelengths.





Fig. 7. (a) Two-photon excited fluorescence spectra of **M4** in DMF ($c = 1 \times 10^{-3} \text{ mol } \text{L}^{-1}$) at 850 nm under different input powers. (b) Logarithmic plot of the output fluorescence integral (I_{out}) of **M4** versus the input laser powers (I_{in}).

3. Conclusion

In conclusion, four novel imidazole derivatives containing different electron donors and acceptors were synthesized by the solvent-free Debus-Radziszewski reaction. Their linear and nonlinear optical properties were systematically investigated in various solvents. Measured by the two-photon induced fluorescence method, **M4** is found to exhibit the largest σ value (1193 GM). The study further demonstrates that the strategies of extending the π -conjugated system, improving the molecular planarity, and possessing the multi-directional charge transfer can enhance the σ value. We believe that the fabrication strategy is potentially applicable to the derivatization of analogous TPA materials.

4. Experimental

4.1. General

1a,³⁷ **2a**,³⁸ **1b**,³⁹ **1c**,⁴⁰ **1d**,⁴¹ and **2d**⁴² were synthesized according to the previous literature procedures. The solvents THF and DMF were disposed by primary procedures before use. Other materials were commercially available, which were used without further purification.

Melting points were measured on an X-4 micromelting point apparatus without correction. ¹H and ¹³C NMR spectra were recorded at room temperature on a Bruker AVANCEIII 500 spectrometer in CDCl₃ or DMSO- d_6 solvent with tetramethylsilane (TMS) as internal standard. FT-IR spectra were measured on KBr pellets with a Thermo Nicolet 6700 spectrometer. Mass spectra were taken on a Therm LCQ TM Deca XP plus ion trap mass spectrometry instrument. Elemental analyses were conducted on a Thermo Finnigan Flash EA 1112 apparatus.

The linear absorption spectra were measured on a Shimadzu UV-2550 UV-visible spectrophotometer. The SPEF spectrum measurements were performed using a RF-5301PC fluorescence spectrophotometer with the maximum absorption wavelengths

as the excitation wavelengths. The TPEF spectra were measured using a femtosecond laser pulse and Ti: sapphire system (680-1080 nm, 80 MHz, 140 fs) as the light source.

The DFT calculations were carried out using the Gaussian 09 program. The nonlocal density function of B3LYP with 6-31G basis sets was used for the calculations.

4.2 4-[(1E)-2-(4-Formylphenyl)ethenyl]benzonitrile (3a)

1a (1.25 g, 6 mmol), **2a** (1.52 g, 6 mmol), and potassium tert-butoxide (0.81 g, 7.2 mmol) in dry THF (25 mL) were added into a dry round-bottom flask under a nitrogen atmosphere with ice bath cooling. The reaction mixture was stirred at room temperature for 12 h and the reaction was monitored by TLC. Then, acetic acid (3.60 g, 60 mmol) in water was added and stirred vigorously. After stirring at room temperature for 6 h, the reaction mixture was neutralized cautiously with saturated aqueous sodium hydrogen carbonate solution, and extracted with CH₂Cl₂ (2×30 mL). The combined organic layers were washed with water (20 mL) and brine (20 mL), dried with anhydrous sodium sulfate, and then filtered. The filtrate was concentrated under vacuum. The crude products were purified by silica gel column chromatography to provide bright yellow crystalline powder (1.25 g). Yield: 89.2%. Mp: 211-213 □. ¹H NMR (CDCl₃, 500MHz) *δ*: 10.04 (s, 1H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.26 (s, 2H).

4.3 4,4'-[(2,5-Dimethoxy-1,4-phenylene)di-(1E)-2,1-ethenediyl]bisbenzaldehyde (3d)

1a (2.08 g, 10 mmol), **2d** (2.19 g, 5 mmol), potassium tert-butoxide (1.23 g, 11 mmol) in dry THF (50 mL), and the synthetic method was similar to that of **3a**. **3d** was obtained as orange-red crystalline powder (1.63 g). Yield: 82.1%; Mp: 230-232 \Box . ¹H NMR (CDCl₃, 500MHz) δ : 10.02 (s, 2H), 7.89 (d, *J* = 8.2 Hz, 4H), 7.71 (d, *J* = 8.2 Hz, 4H), 7.67 (d, *J* = 16.5 Hz, 2H), 7.21 (d, *J* = 16.5 Hz, 2H), 7.18 (s, 2H), 3.98 (s, 6H)

4.4 4-[(1E)-[2-[4-(4,5-Diphenyl-1H-imidazol-2-yl)phenyl]ethenyl] benzonitrile (M1)

Benzil (0.21 g, 1 mmol), 3a (0.23 g, 1 mmol), acidic alumina (1.02 g, 10 mmol), and

ammonium acetate (0.39 g, 5 mmol) were ground into powder in a mortar, and then heated in a thermostatic reactor at 110°C for 10 h. After completion of the reaction confirmed by TLC, the reaction mixture was treated with water to furnish the crude products. Further purification was done by silica gel column chromatography to provide **M1** as yellow needle crystals (0.34 g). Yield: 81.4%; Mp: 294-296 \square ; ¹H NMR (DMSO-*d*₆, 500MHz) δ : 12.77 (s, 1H), 8.13 (d, *J* = 8.3 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 7.5 Hz, 2H), 7.53 (d, *J* = 16.5 Hz, 1H), 7.52 (d, *J* = 7.7 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.44 (d, *J* = 16.5 Hz, 1H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H); ¹³C NMR (DMSO-*d*₆, 500MHz) δ : 145.14, 141.86, 137.44, 136.14, 135.09, 132.63, 131.70, 130.99, 130.11, 128.66, 128.54, 128.45, 128.19, 127.84, 127.36, 127.13, 127.09, 127.03, 126.58, 125.45, 119.03, 109.48; FT-IR (KBr) *v*: 3398, 3028, 2226, 1598, 1504, 1490, 1439, 1174, 964, 841, 765, 697, 559 cm⁻¹; ESI-MS *m/z*: 424.2 [M+H]⁺; HRESI-MS calcd for C₃₀H₂₂N₃ [M+H]⁺: 424.1814; found: 424.1823; Anal. calcd for C₃₀H₂₁N₃: C 85.08, H 5.00, N 9.92; found C 85.27, H 5.13, N 10.18.

4.5 9-[4-(4,5-Diphenyl-1H-imidazol-2-yl)phenyl]- 9H-carbazole (M2)

The compound was synthesized by the same procedure described for **M1** using **1b**, benzil, acidic alumina and ammonium acetate as the starting materials. **M2** was obtained as white crystalline powder. Yield: 85.6%; Mp: 302-303 \Box ; ¹H NMR (DMSO-*d*₆, 500MHz) δ : 12.90 (s, 1H), 8.39 (d, *J* = 8.4 Hz, 2H), 8.28 (d, *J* = 7.8 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 7.4 Hz, 2H), 7.56 (d, *J* = 7.4 Hz, 2H), 7.47-7.50 (m, 6H), 7.41 (t, *J* = 7.3 Hz, 1H), 7.31-7.36 (m, 4H), 7.26 (t, *J* = 7.3 Hz, 1H); ¹³C NMR (DMSO-*d*₆, 500MHz) δ : 144.86, 140.00, 136.58, 129.40, 128.45, 127.07, 126.82, 126.31, 122.84, 120.55, 120.17, 109.75; FT-IR (KBr) *v*: 3420, 3059, 1601, 1494, 1451, 1316, 1230, 750, 697 cm⁻¹; ESI-MS *m*/*z*: 462.2 [M+H]⁺; HRESI-MS calcd for C₃₃H₂₄N₃ [M+H]⁺: 462.1970; found: 462.1984; Anal. calcd for C₃₃H₂₃N₃: C 85.87, H 5.02, N 9.10; found C 85.96, H 5.09, N 9.21.

4.6 3,6-Bis(4,5-diphenyl-1H-imidazol-2-yl) -9-ethyl-9H-carbazole (M3)

The compound was synthesized by the same procedure described for **M1** using **1c**, benzil, acidic alumina and ammonium acetate as the starting materials. **M3** was obtained as white crystalline powder. Yield: 83.9%; Mp >300 \Box ; ¹H NMR (DMSO-*d*₆, 500MHz) δ : 12.66 (s, 2H), 8.98 (d, *J* = 1.3 Hz, 2H), 8.27 (dd, *J*₁ = 8.6 Hz, *J*₂ = 1.5 Hz, 2H), 7.76 (d, *J* = 8.6 Hz, 2H), 7.62 (d, *J* = 7.2 Hz, 4H), 7.56 (d, *J* = 7.2 Hz, 4H), 7.47 (t, *J* = 7.6 Hz, 4H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 4H), 7.24 (t, *J* = 7.3 Hz, 2H), 4.53 (q, 2H), 1.40 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (DMSO-*d*₆, 500MHz) δ : 146.66, 140.04, 136.88, 135.45, 131.34, 128.65, 128.31, 128.17, 127.69, 127.57, 127.11, 126.41, 123.75, 122.50, 121.93, 117.24, 109.60, 37.36, 13.92; FT-IR (KBr) *v*: 3411, 3055, 2975, 1605, 1484, 1450, 1382, 1295, 1226, 1127, 1072, 767, 703 cm⁻¹; ESI-MS *m*/*z*: 632.4 [M+H]⁺, 316.8 [M+2H]²⁺; HRESI-MS calcd for C₄₄H₃₄N₅ [M+H]⁺: 632.2814; found: 632.2831; Anal. calcd for C₄₄H₃₃N₅: C 83.65, H 5.26, N 11.09; found C 83.91, H 5.41, N 11.26.

4.7 2,2'-[(2,5-Dimethoxy-1,4-phenylene)bis[(1E)-2,1-ethenediyl-4,1-phenylene]]bis(4,5

-diphenyl-1H-imidazole) (M4)

The compound was synthesized by the same procedure described for **M1** using **3d**, benzil, acidic alumina and ammonium acetate as the starting materials. **M4** was obtained as orange-yellow crystalline powder. Yield: 76.5%; Mp >300 \Box ; ¹H NMR (DMSO-*d*₆, 500MHz) δ : 12.85 (bs, 2H), 8.12 (d, *J* = 8.3 Hz, 4H), 7.72 (d, *J* = 8.3 Hz, 4H), 7.54 (d, *J* = 7.4 Hz, 8H), 7.53 (d, *J* = 16.5 Hz, 2H), 7.42 (d, *J* = 16.5 Hz, 2H), 7.39 (s, 2H), 7.33-7.44 (m, 12H), 3.95 (s, 6H); ¹³C NMR (DMSO-*d*₆, 500MHz) δ : 151.12, 149.17, 145.31, 137.31, 135.13, 131.03, 129.61, 129.26, 128.65, 128.41, 128.19, 127.78, 127.08,126.87, 126.73, 125.86, 125.52, 122.84, 115.11, 109.33, 56.18; FT-IR (KBr) *v*: 3401, 3050, 2934, 2829, 1602, 1492, 1448, 1406, 1208, 1043, 967, 764, 696 cm⁻¹; ESI-MS *m/z*: 779.4 [M+H]⁺, 390.5 [M+2H]²⁺; HRESI-MS calcd for C₅₄H₄₃N₄O₂ [M+H]⁺:

779.3386; found: 779.3405; Anal. calcd for C₅₄H₄₂N₄O₂: C 83.26, H 5.43, N 7.19; found C 83.53, H 5.61, N 7.45.

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Supplementary data

Supplementary data (1H NMR, 13C NMR, and MS spectra of M1-M4.) can be found in the supporting information.

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