Donor–Acceptor Materials Exhibiting Thermally Activated Delayed Fluorescence Using a Planarized N-Phenylbenzimidazole Acceptor

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Supporting Information

ABSTRACT: An *N*-phenylbenzimidazole constrained in a coplanar fashion with a methylene tether (IMAC) was designed and used to prepare a series of emitters exhibiting thermally activated delayed fluorescence (TADF). Four novel TADF emitters using 9,9-dimethylacridine, phenoxazine, phenothiazine, and bis(di-*p*-tolylamino)carbazole as the donor group were designed and synthesized using IMAC as the acceptor. Additionally, two deepblue fluorescent emitters were prepared with carbazole and tercarbazole as the donor moieties. The twisted conformation



between donor and acceptor in these molecules resulted in effective spatial separation of the HOMO and LUMO and small singlet-triplet energy gaps. Crystallographic properties, electronic structures, thermal stabilities, photophysical properties, and energy levels were studied systematically. Ultimately, these findings provide a promising opportunity for the design and synthesis of highly efficient TADF materials based on IMAC derivatives.

INTRODUCTION

The discovery of thermally activated delayed fluorescence (TADF) has revolutionized organic light-emitting diode (OLED) technology, enabling the fabrication of OLEDs with 100% internal quantum efficiencies using purely organic emitters.^{1–5} Capable of converting triplet excitons to singlets through reverse intersystem crossing (RISC), TADF compounds have attracted significant recent attention as robust, efficient, and scalable emissive materials.^{6–10} Though applications in OLEDs have been the primary driver of TADF research to date, these materials have also found use in fluorescence lifetime imaging^{11,12} and oxygen sensing.¹³ To achieve efficient RISC, TADF materials are typically designed to minimize the energy difference between the lowest triplet (T_1) and lowest singlet (S_1) excited states, termed ΔE_{ST} .

While T_1 states are substantially lower in energy than their S_1 counterparts in the vast majority of molecules, a small ΔE_{ST} can be achieved by minimizing the Pauli repulsion (or exchange energy) between ground and excited state electrons. In practical terms, this is commonly achieved by designing materials with minimal overlap between their HOMO and LUMO, such that the electrons of the frontier orbitals will occupy different regions of space when the material is excited. This is often obtained by the coupling of donor and acceptor units in a twisted conformation,^{14–16} sometimes using steric bulk to ensure that the π systems of the donor and acceptor remain orthogonal.¹⁷ This type of conformation also results in emitters with large transition dipoles and significant charge-

transfer character, including broad emission bands and large Stokes shifts.

More recently, several studies have demonstrated that molecular rigidification can lead to narrower emission spectra, higher quantum yields and enhanced stability in luminescent materials, primarily as a result of suppressed vibrational motion.^{18,19} For example, Yamaguchi and co-workers utilized the idea of structural constraint to create an extremely photostable phosphole-based dye for multiple-acquisition stimulated emission depletion (STED) imaging.^{20,21} Furthermore, they synthesized a series of planarized 9-phenylanthracene derivatives, in which the planar and rigid structure induced effective π -conjugation and reduced the nonradiative decay process from the excited state, resulting in red-shifted absorptions, increased molar absorption coefficients, and intense fluorescence.^{22–26} Hatakeyama and co-workers have also leveraged an organoboron compound, possessing two nitrogen atoms, in a rigid polycyclic aromatic framework to produce ultrapure blue TADF emitters in this fashion.^{4,18,19}

Deep blue or violet TADF emitters pose a particular synthetic challenge, in light of the large Stokes shifts typically caused by the common donor–acceptor conformation of TADF materials.^{27–33} To realize deep blue emission a wide energy gap >2.75 eV is required; therefore, an electron

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acceptor with a shallow LUMO is ideal. Imidazole and benzimidazole are attractive electron acceptors for this reason, and many imidazole-based blue fluorescent emitters have been reported with PLQYs near unity and high device efficiencies.^{34–37} However, there are few reports in which imidazole-containing compounds have exhibited TADF. In 2018, Wang and co-workers³⁸ reported highly efficient green organic light emitting diodes with phenanthroimidazole-based TADF emitters, and shortly after Kido and co-workers reported a series of imidazo[1,2-f]phenanthridine-based sky-blue TADF compounds.³⁹

Herein we report the design of a planarized 1-phenylbenzimidazole chromophore that has been linked via a methylene bridge at the 2 and 7 positions of the phenyl ring and the benzimidazole, respectively (Figure 1). This fused



Figure 1. Optimized structure for 1-phenyl-1*H*-benzo[*d*]imidazole (left) and 6,6-dimethyl-6*H*-imidazo[4,5,1-de]acridine (right).

imidazole/acridine chromophore (IMAC, formally 6,6-dimethyl-6*H*-imidazo[4,5,1-de]acridine) was then used to prepare



donor- π -acceptor materials using six different donor moieties commonly used in organic electronics, including phenoxazine (PXZ), phenothiazine (PTZ), 9,9-dimethylacridan (ACR), and carbazole (CZ). Several of these molecules exhibit TADF with deep blue to green emission colors, and quantum yields of up to 0.99. These compounds should find application in the emitting layer of OLEDs, either as the emitter or as ambipolar host materials.

RESULTS AND DISCUSSION

Synthesis and Solid-State Structure. Synthesis of the IMAC acceptor fragment began with a double Grignard addition to methyl anthranilate using MeMgBr to give tertiary alcohol 1, which was then protected using 1,1'-carbonyldiimidazole to give carbamate 2 (Scheme 1). Nucleophilic aromatic substitution of o-nitrofluorobenzene with 2 was then used to obtain 3 in 70% yield. Hydrolysis of the carbamate was achieved in the presence of NaOH, followed by electrophilic aromatic substitution in the presence of H_3PO_4 to form the nitrosylated acridine 5. Reduction of the nitro group to a primary amine was achieved using Pd/C and hydrazine, yielding 6 quantitatively and giving a planarized, ortho-diamine that can be used to prepare benzimidazoles from a variety of aldehydes. Finally, a series of phenylaldehyde-linked donors were coupled with 6 via I2-mediated intramolecular C-H amidation⁴⁰ to synthesize the target donor- π -acceptor compounds in yields ranging from 56% to 65%. The identity of final compounds was confirmed by ¹H and ¹³C{¹H} NMR, as well as high resolution mass spectrometry (HRMS).

Single crystals of PXZ-IMAC, PTZ-IMAC, ACR-IMAC, and CZ-IMAC were obtained from a mixture of CH_2Cl_2 and



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Figure 2. Crystal structures of (A) **PXZ-IMAC**, (B) **PTZ-IMAC**, (C) **ACR-IMAC**, and (D) **CZ-IMAC** depicted with 50% thermal ellipsoids. Hydrogen atoms and cocrystallized solvent molecules omitted for clarity. Selected bond lengths (Å): **PXZ-IMAC** N1–C16 1.319(2), N2–C16 1.397(3), N3–C20 1.437(3); **PTZ-IMAC** N1–C16 1.318(3), N2–C16 1.396(2), N3–C20 1.437(2); **ACR-IMAC** N1–C16 1.326(3), N2–C16 1.400(3), N3–C20 1.436(3); **CZ-IMAC** N1–C16 1.318(3), N2–C16 1.392(2), N3–C20 1.428(2). Selected torsion angles (deg): **PXZ-IMAC** N1–C16–C17–C18 135.0(2), C19–C20–N3–C23 98.7(2); **PTZ-IMAC** N1–C16–C17–C18 57.5(3), C19–C20–N3–C23 69.3(2); **ACR-IMAC** N1–C16–C17–C18 134.2(2), C19–C20–N3–C23 97.6(3); **CZ-IMAC** N1–C16–C17–C18 52.5(3), C19–C20–N3–C23 120.0(2).



Figure 3. UV–vis spectra measured in CH_2Cl_2 at 1×10^{-5} M and PL spectra measured in toluene solution at 0.05 to 0.15 optical density for (A) **PXZ-IMAC**, (B) **PTZ-IMAC**, (C) **ACR-IMAC**, (D) **CZ-IMAC**, (E) **TerCZ-IMAC**, and (F) **TolCZ-IMAC**. Photographs of the series of compounds in toluene (G) and as 10 wt % films in DPEPO (H) irradiated with 365 nm light.

hexanes by slow evaporation (Figure 2). The solid-state structures indicate the donor groups are twisted with respect to the phenyl ring giving very large dihedral angles of 81.3 and 82.4° for PXZ-IMAC and ACR-IMAC, respectively. PTZ-IMAC and CZ-IMAC have more moderated twisting with dihedral angles of 69.3 and 60.0°, respectively. Such twisted structures typically result from the steric repulsion of hydrogen atoms in the phenyl and heteroaromatic units. Further, it results in effective spatial separation of the HOMO and LUMO and reduction of ΔE_{ST} . There also exists a moderate twist between the imidazole plane and the phenyl ring resulting in dihedral angles between 52.5–57.5°. PXZ-IMAC, PTZ-IMAC, and ACR-IMAC all pack in the P21/c space group, while CZ-IMAC packs in the $P\overline{1}$ space group. Additionally, the

CZ-IMAC derivative is the only compound to cocrystallize with solvent (CH_2Cl_2) .

Photophysical and Electrochemical Properties. UV– vis absorption and photoluminescence (PL) spectra of this series of compounds in toluene solution $(1 \times 10^{-5} \text{ M})$ are shown in Figure 3. Absorption maxima are between 293 and 308 nm, and all compounds have broad, featureless emission spectra consistent with a charge-transfer excited state. On the basis of TD-DFT calculations we attribute the lowest energy transition in all cases to the HOMO to LUMO transition. TD-DFT predicts **PXZ-IMAC**, **PTZ-IMAC**, **ACR-IMAC**, and **ToICZ-IMAC** to all have lowest energy transitions above 395 nm, significantly higher than the **CZ-IMAC** or **TerCZ-IMAC** derivatives (Table S1). However, the oscillator strengths are calculated to be 0.0004 (extremely low) for the **PTZ-IMAC**



Figure 4. PL decay curves for (A) PXZ-IMAC, (B) PTZ-IMAC, (C) ACR-IMAC, (D) CZ-IMAC, (E) TerCZ-IMAC, and (F) TolCZ-IMAC doped in 10 wt % DPEPO films at 300 K.

Table 1. Ph	notophysical	Properties	of IMAC	Compounds
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entry	$\lambda_{ m max,abs}^{a}$	$\lambda_{\max,em}^{b,c}$	Φ solution ^b /solid ^c	CIE ^b	$\tau_{\rm p} \ ({\rm ns})^c$	$ au_{\rm d} \ (\mu { m s})^c$
PXZ-IMAC	298	502/485	0.31/0.71	(0.23, 0.43)	4.2, 13.8	1390
PTZ-IMAC	303	515/469	0.08/0.05	(0.27, 0.44)	2.1, 10.1	228
ACR-IMAC	293	450/449	0.34/0.51	(0.15, 0.12)	5.7, 14.2	127
CZ-IMAC	293	394/405	0.99/0.85	(0.16, 0.03)	1.9, 28.2	_
TerCZ-IMAC	294	401/409	0.94/0.61	(0.16, 0.04)	2.9, 17.2	_
TolCZ-IMAC	308	496/491	0.85/0.45	(0.21, 0.39)	4.4, 13.1	1194
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^aMeasured in CH₂Cl₂. ^bMeasured in degassed toluene with an optical density between 0.05 and 0.15. ^cMeasured as films doped in DPEPO at 10 wt % under vacuum. DPEPO: Bis[2-(diphenylphosphino)phenyl] ether oxide.

and 0.0002 for the ACR-IMAC derivatives, slightly higher at 0.0142 for the PXZ-IMAC derivative and much higher at 0.2792 for the TolCZ-IMAC derivative, consistent with apparent intensities observed in their experimental spectra. All compounds showed strong positive solvatochromism in the fluorescence spectra, with significant red shifts in polar relative to nonpolar solvents (Figure S31). The effect was most pronounced for TolCZ-IMAC and PXZ-IMAC, with red shifts of 176 (5861 cm^{-1}) and 157 nm (5510 cm^{-1}) going from hexanes to MeCN, respectively. CZ-IMAC had the least dramatic shift of 3676 cm⁻¹ going from 378 to 439 nm as the solvent polarity was increased from hexanes to MeCN. For simplicity Stokes shifts discussed in this paper are the apparent shifts from the largest absorption band to the emission maxima. It has previously been reported that chromophores containing N-phenylphenothiazine can adopt two conformations, termed quasi-axial and quasi-equatorial, differing in the relative orientations of the phenothiazine moiety and the phenyl ring.41-44 Such conformers often result in dual emission properties, as is observed in PTZ-IMAC, with peaks at ~400 and ~530 nm and may also explain its low photoluminescence quantum yield (PLQY, Φ).

In order to probe the delayed fluorescence behavior of the series of compounds, transient photoluminescence decay curves for each compound doped in bis[2-(diphenylphosphino)phenyl] ether oxide (DPEPO) films (10 wt %) were measured at room temperature. DPEPO was chosen since it is a large band gap material commonly used to host blue TADF materials in OLEDs. As shown in Figure 4 and summarized in Table 1, the doped films of **PXZ-IMAC**, **PTZ-IMAC**, **ACR**-

IMAC, and TolCZ-IMAC showed clear long-lived exponential decays at 300 K. PXZ-IMAC exhibits a two-component short lifetime of 4.2 and 13.8 ns (Figure S32) and a long lifetime of 1390 µs, and these are 2.1 ns, 10.1 ns and 228 µs for PTZ-IMAC. ACR-IMAC and TolCZ-IMAC had lifetimes of 5.7 ns, 14.2 ns, 127 μ s and 4.4 ns, 13.1 ns, 1194 μ s, respectively. The two-component nature of the short lifetimes is likely a result of the film consisting of both an IMAC emitter and DPEPO host; thus, there is possibility for direct excitation of the emitter as well as for energy transfer from the host to emitter. The short lifetime component was attributed to relaxation from S_1 to S_0 , and the delayed component was assigned to thermal upconversion of excitons from T_1 to S_1 , followed by relaxation from S_1 to S_0 . PL decay curves were measured for **PXZ-IMAC**, PTZ-IMAC, ACR-IMAC, and TolCZ-IMAC at 77 K, and in all cases the delayed component was suppressed, confirming the thermal dependence (Figure S33). Time-resolved emission spectra of all compounds were obtained in 2-MeTHF solution measured at 77 K (Figure \$34) in order to determine the singlet-triplet gap for each compound. ΔE_{ST} was also determined for doped films at room temperature by using an approximate relationship among ΔE_{ST} , k_{TADF} , and k_{F} (Table S2), as described by Adachi^{5,45} and Hatakeyama.¹⁹ We also note that the delayed fluorescence lifetimes for TolCZ-IMAC and PXZ-IMAC are much longer than those of PTZ-IMAC and ACR-IMAC, while their solid-state quantum yields are significantly higher (Table 1). Films of CZ-IMAC and TerCZ-IMAC had no observable delayed component under these conditions, consistent with DFT calculations indicating these compounds possess a larger ΔE_{ST} (vide infra).

Table 2	2.	Calculated	and	Experimental	Electronic	Properties	of the	Series	of IMAC	Compounds
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			HOMO (eV)		LUMO (eV)		E_g (eV)		$\Delta E_{ m ST}$ (eV)	
compound	$E_{1/2}^{\text{ox }a}$	$E_{1/2}^{\text{red }a}$	calc.	exp. ^b	calc.	exp. ^b	calc.	exp. ^c	calc.	exp. ^{d,e}
PXZ-IMAC	0.28	-2.52	-4.90	-5.08	-1.41	-2.28	2.77	2.92	0.03	0.29/0.27
PTZ-IMAC	0.31	-2.52	-5.23	-5.11	-1.40	-2.28	3.12	3.32	0.04	0.25/0.76
ACR-IMAC	0.51	-2.52	-5.15	-5.31	-1.34	-2.28	3.06	3.15	0.01	0.21/0.25
CZ-IMAC	0.49	-2.54	-5.63	-5.29	-1.33	-2.26	3.65	3.41	0.60	-/0.71
TerCZ-IMAC	-	-2.45	-5.43	-5.61^{f}	-1.54	-2.35	3.43	3.35	0.31	-/0.66
TolCZ-IMAC	0.21	-2.48	-4.71	-5.01	-1.33	-2.32	2.93	2.92	0.17	0.27/0.28

^{*a*}In DMF relative to FeCp^{0/+}. ^{*b*}Calculated from $E_{1/2}^{\text{ox}}$ relative to the FeCp^{0/+} HOMO level (-4.80 eV). ^{*c*} E_{g} was determined from the intersection point of the normalized emission and absorption spectra. ^{*d*}Determined using an approximate relationship among ΔE_{ST} , k_{TADF} , and k_{F} in the same manner as reported by Adachi in refs 45 and 5 and by Hatakeyama in ref 19. For additional information see Table S2. ^{*c*}Determined from the high energy band edge of the phosphorescence spectrum in 2-MeTHF at 10⁻⁵ M at 77 K. ^{*f*}Calculated from the LUMO level and the optical energy gap, E_{g} .



Figure 5. Optimized structures, and HOMO and LUMO distributions for the series of IMAC-containing compounds.

The electrochemical properties and energy levels of these compounds were investigated by cyclic voltammetry in DMF using a conventional three electrode system. All compounds undergo reduction at approximately –2.50 eV (Table 2 and Figure S35) relative to the FeCp^{0/+} redox couple, arising from the IMAC unit. These are in reasonable agreement with similar donor–acceptor compounds containing benzimidazole.³⁷ The LUMO energy levels of the compounds were calculated to be approximately –1.4 eV. ToICZ-IMAC had the lowest oxidation potential at 0.21 eV, followed closely by PXZ-IMAC at 0.28 eV and PTZ-IMAC at 0.31 eV. CZ-IMAC and ACR-IMAC had significantly higher oxidation potentials at 0.49 and 0.51 eV, respectively. Oxidation of the TerCZ-IMAC could not be achieved within the solvent window of DMF, though a reduction peak was still observed for this compound.

Theoretical Calculations. Quantum chemical calculations using density functional theory (DFT) with the PBE0/6-

31+G(d) method/basis set in Gaussian 09 software were performed to obtain insight into the molecular conformation and electronic structures of these emissive materials. The calculation results, showing the optimized structure and HOMO/LUMO distribution of each compound, are given in Figure 5. Significant separation of the HOMO and LUMO is present for all compounds, with the HOMO mainly distributed on the donor group and the LUMO centered on the IMAC acceptor. CZ-IMAC was an exception to this trend, with the IMAC unit contributing significantly to the HOMOconsistent with the lack of observed delayed fluorescence for this material. We next calculated the S1 and T1 excited state energies using time-dependent density functional theory (TD-DFT). The calculated ΔE_{ST} values were <0.04 eV for PXZ-IMAC, PTZ-IMAC, and ACR-IMAC, consistent with their apparent TADF behavior. CZ-IMAC was calculated to have quite a large ΔE_{ST} of 0.60 eV, most likely due to the very weak

donating ability of the CZ donor moiety leading to substantial overlap of the HOMO and LUMO on the IMAC fragment. TerCZ-IMAC and TolCZ-IMAC were calculated to have gaps of 0.31 and 0.17 eV, respectively. These values are small enough that efficient TADF should be possible.

CONCLUSIONS

In summary, a planarized IMAC acceptor fragment was prepared and used to synthesize six donor- π -acceptor type emissive materials. Four of these donor- π -acceptor molecules exhibit TADF with deep blue to green emission color in the solid state and photoluminescence quantum yields of up to 0.85 in solution. Additionally, two fluorescent emitters were prepared with carbazole and tercarbazole donor moieties and quantum yields of 0.94 and 0.99, respectively. Theoretical calculations established the donor-acceptor character of the molecules, as well as indicating small $\Delta E_{\rm ST}$ values for the compounds that exhibited delayed fluorescence. The results provide a promising opportunity for the design and synthesis of highly efficient TADF materials based on IMAC derivatives.

EXPERIMENTAL DETAILS

General Considerations. All reactions and manipulations were carried out under a nitrogen atmosphere using standard Schlenk or glovebox techniques unless otherwise stated. Dry solvents were obtained from Caledon Laboratories, dried using an Innovative Technologies Inc. solvent purification system, collected under vacuum, and stored under a nitrogen atmosphere over 4 Å molecular sieves. All reagents were purchased from Sigma-Aldrich, Cambridge Isotope Laboratories, Alfa Aesar or Tokyo Chemical Institute and used as received unless otherwise stated. Syntheses of the following compounds have been previously reported: 1,46 4-(10H-phenoxazin-10-yl)benzaldehyde,⁴⁷ 4-(10*H*-phenothiazin-10-yl)benzaldehyde,⁴⁴ 4-(9*H*-carbazol-9-yl)benzaldehyde,⁴⁸ 4-(9'*H*-[9,3':6',9"-tercarbazol]-9'yl)benzaldehyde,⁴⁹ and 9-benzyl-3,6-diiodo-9*H*-carbazole.⁴⁹ The ¹H and ¹³C{¹H} nuclear magnetic resonance (NMR) spectra were measured on a Bruker AV III HD 400 MHz spectrometer with chloroform-d (CDCl₃), methylene chloride- d_2 (CD₂Cl₂), benzene- d_6 (C_6D_6) or dimethyl sulfoxide- d_6 (DMSO- d_6) as the solvent. The chemical shift data are reported in units of δ (ppm) relative to residual solvent. Absorbance measurements were made on a Cary 60 spectrometer and fluorescence measurements were made on an Edinburgh Instruments FS5 spectrofluorometer. Absolute photoluminescence quantum yields were determined using an Edinburgh Instruments SC-30 Integrating Sphere Module; toluene was used as the solvent and spectra obtained at approximately 10^{-5} M unless otherwise stated. Photoluminescence decay characteristics of the film samples were investigated under vacuum conditions using an Edinburgh Instruments FS5 spectrofluorometer and SC-80 sample holder. The fast decay component was recorded using time-correlated single photon counting in conjunction with a 313 nm EPLED excitation source, while the slow decay component was recorded using multichannel scaling with a pulsed Xe flash lamp source. Low temperature time-resolved emission spectra were measured on a Horiba PTI QM-400 spectrometer equipped with a Continuum PL8000 ns YAG laser, operating at 355 nm, 10 Hz, and 1-2 mJ/ pulse. Mass spectra were recorded on a Kratos MS-50 instrument using electron impact ionization. Melting points (mp) were determined using a Barnstead Electrotherm 1001D/1001 Mel-Temp capillary melting point apparatus equipped with a Fluke 51-II digital thermometer.

Electrochemical Methods. Cyclic voltammograms were recorded using a BASi Epsilon Eclipse potentiostat at room temperature using a standard three-electrode configuration (working electrode: 3 mm diameter glassy carbon; reference electrode: RE-5B Ag/AgCl electrode in saturated aqueous KCl (BASi Inc.), referenced externally to ferrocene/ferrocenium (0.543 V in DMF);⁵⁰ counter electrode: Pt

wire) in 0.1 M tetrabutylammonium hexafluorophosphate in DMF. Experiments were run at a scan rate of 100 mV s⁻¹ in dry degassed electrolyte solution with ~1 mg mL⁻¹ of analyte.

Density Functional Theory. Calculations were performed using the Gaussian 09 software package.⁵¹ Ground state geometries and energies were calculated at the PBE0/6-31+G(d) level of theory. The singlet and triplet states were calculated by the Tamm-Dancoft approximation to time-dependent density functional theory (TD-DFT) with the PBE0 functional at the same basis set level. Molecular orbitals were visualized using Avogadro version 1.20 and rendered using POV-Ray version 3.7.0.

Synthetic Procedures. Synthesis of 4,4-Dimethyl-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (2). A mixture of N,N'-carbonyldiimidazole (24.4 g, 150 mmol) and 2-(2-aminophenyl)propan-2ol (1) (18.0 g, 119 mmol) in THF (500 mL) was refluxed for 16 h. The solvent was evaporated under reduced pressure to give a yellow oil, which was redissolved in CH₂Cl₂ and washed with saturated aqueous NH₄Cl, 2 N HCl solution, and brine. The organic layer was dried over anhydrous MgSO₄ and concentrated to afford a yellow solid. Yield = 17.8 g (85%). mp = 106.5–108.6 °C. ¹H NMR (400 MHz, DMSO-d₆) δ 10.20 (s, 1H), 7.32–7.19 (m, 2H), 7.04 (td, *J* = 7.6, 1.2 Hz, 1H), 6.91 (dd, *J* = 7.9, 1.1 Hz, 1H), 1.62 (s, 6H). ¹³C NMR (101 MHz, DMSO-d₆) δ 150.66, 134.67, 128.61, 126.23, 123.41, 122.57, 113.99, 81.32, 27.62. HRMS (EI) m/z [M^{+•}] calcd for [C₁₀H₁₁NO₂]^{+•}, 177.07898; found, 177.07862; difference, -2.02 ppm.

Synthesis of 4,4-Dimethyl-1-(2-nitrophenyl)-1,4-dihydro-2Hbenzo[d][1,3]oxazin-2-one (3). A mixture of 2 (17.8 g, 100 mmol), 1-fluoro-2-nitrobenzene (15.7 g, 111 mmol) and CsCO₃ (39.1 g, 121 mmol) in DMF (250 mL) was heated to 95 °C for 16 h. After cooling to room temperature, the reaction was poured into 500 mL of water and extracted with EtOAc ($5 \times 100 \text{ mL}$). The combined organic layer was washed with water and brine, dried over anhydrous MgSO₄, concentrated to give a bright yellow oil, and then purified through silica gel column chromatography (hexanes/EtOAc 4:1, $R_f = 0.02$ gradient to hexanes/EtOAc 1:1) to afford a yellow solid. mp = 89.8-91.7 °C. Yield = 21.1 g (70%). ¹H NMR (400 MHz, DMSO- d_6) δ 8.29 (dd, J = 8.2, 1.5 Hz, 1H), 7.96 (td, J = 7.7, 1.5 Hz, 1H), 7.83 (td, *J* = 7.8, 1.4 Hz, 1H), 7.76 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.47 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.22 (dtd, J = 24.3, 7.6, 1.4 Hz, 2H), 6.31 (dd, J = 8.0, 1.2 Hz, 1H), 1.81 (s, 3H), 1.78 (s, 3H). ¹³C NMR (101 MHz, DMSO- d_6) δ 149.60, 146.94, 136.35, 135.36, 131.95, 130.58, 130.23, 128.90, 127.74, 125.81, 123.84, 123.78, 114.60, 82.02, 28.11, 27.15. HRMS (EI) m/z [M^{+•}] calcd for [C₁₆H₁₄N₂O₄]^{+•}, 298.09536; found, 298.09503; difference, -1.08 ppm.

Synthesis of 2-{2-[(2-Nitrophenyl)amino]phenyl}propan-2-ol (4). A mixture of 3 (21.0 g, 70.4 mmol) and 5% aqueous NaOH (10 g NaOH in 200 mL water) in EtOH (300 mL) was heated to reflux for 16 h. The reaction mixture turned from light yellow to dark red. The solvent was partially removed under reduced pressure before the mixture was poured into 500 mL of water, sonicated for 15 min, and the resulting bright orange powder collected by vacuum filtration. Yield = 12.4 g (64%). mp = 129.5–131.0 °C. ¹H NMR (400 MHz, DMSO- d_6) δ 10.06 (s, 1H), 8.05 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.85 (dt, *J* = 7.6, 1.1 Hz, 1H), 7.53–7.45 (m, 1H), 7.29–7.15 (m, 2H), 7.10–6.93 (m, 2H), 1.58 (s, 6H). ¹³C NMR (101 MHz, DMSO- d_6) δ 135.51, 135.05, 133.04, 132.86, 131.67, 129.04, 127.10, 125.44, 123.96, 122.80, 118.89, 116.16, 36.24, 31.40. HRMS (EI) m/z [M⁺⁺] calcd for [C₁₅H₁₆N₂O₃]^{+•}, 272.11609; found, 272.11664; difference, 2.03 ppm.

Synthesis of 9,9-Dimethyl-4-nitro-9,10-dihydroacridine (5). A suspension of 4 (12.4 g, 45.5 mmol) in H_3PO_4 (200 mL) was stirred for 16 h. The reaction mixture turned from orange to dark red. The mixture was poured into water (500 mL) and the resulting bright red powder collected by vacuum filtration. Yield = 9.7 g (84%). mp = 134.1–135.6 °C. ¹H NMR (400 MHz, DMSO- d_6) δ 10.05 (s, 1H), 8.04 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.83 (dt, *J* = 7.5, 1.1 Hz, 1H), 7.48 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.27–7.15 (m, 2H), 7.05 (ddd, *J* = 8.4, 7.1, 1.5 Hz, 1H), 6.99 (dd, *J* = 8.5, 7.5 Hz, 1H), 1.56 (s, 6H). ¹³C NMR (101 MHz, DMSO- d_6) δ 135.51, 135.03, 133.01, 132.85, 131.64, 129.04,

127.10, 125.42, 123.94, 122.80, 118.88, 116.14, 36.22, 31.36. HRMS (EI) m/z [M^{+•}] calcd for [C₁₅H₁₄N₂O₂]^{+•}, 254.10553; found, 254.10452; difference, -3.96 ppm.

Synthesis of 9,9-Dimethyl-9,10-dihydroacridin-4-amine (6). A mixture of 5 (143 mg, 0.562 mmol) in EtOH (5 mL) was cooled to 0 °C and placed under a flow of N₂ gas. Pd/C (6 mg, 0.06 mmol) was added to the stirred solution followed by very slow addition of N2H4. The mixture was stirred for 30 min then slowly allowed to warm to room temperature (care was taken to ensure the reaction vessel was not overpressurizing) followed by heating to 50 °C. After 2 h the reaction was cooled to room temperature and subsequently filtered using EtOH to rinse. The filtrate was collected and concentrated to give a black solid. Yield = 123 g (99%). mp = 108.2-110.6 °C. ¹H NMR (400 MHz, DMSO- d_6) δ 7.80 (s, 1H), 7.34 (d, J = 7.8 Hz, 1H), 7.07 (t, J = 7.5 Hz, 1H), 6.94 (dd, J = 8.0, 1.3 Hz, 1H), 6.82 (t, J = 7.5 Hz, 1H), 6.70 (d, J = 7.7 Hz, 1H), 6.63 (t, J = 7.7 Hz, 1H), 6.53 (dd, J = 7.6, 1.4 Hz, 1H), 4.87 (s, 2H), 1.48 (s, 6H). ¹³C NMR (101 MHz, DMSO-d₆) δ 139.07, 133.30, 128.14, 128.10, 126.31, 125.53, 125.14, 119.82, 119.41, 113.78, 113.69, 112.60, 35.64, 30.74. HRMS (EI) m/z $[M^{+\bullet}]$ calcd for $[C_{15}H_{16}N_2]^{+\bullet}$, 224.13135; found, 224.13112; difference, -1.00 ppm.

Synthesis of 10-[4-(6,6-Dimethyl-6H-imidazo[4,5,1-de]acridin-1yl)phenyl]-10H-phenoxazine (PXZ-IMAC). A mixture of 5 (100 mg, 0.446 mmol) and 4-(10H-phenoxazin-10-yl)benzaldehyde (141 mg, 0.491 mmol) in EtOH (10 mL) was refluxed for 16 h. The solvent was evaporated under reduced pressure to give a yellow oil, which was redissolved in CH₂Cl₂ (10 mL), followed by the sequential addition of iodine (135 mg, 0.532 mmol) and K₂CO₃ (185 mg, 1.34 mmol). The reaction mixture was stirred at reflux temperature for another 16 h. Upon completion of the reaction, it was guenched with 5% $Na_2S_2O_3$ (20 mL) and then extracted with CH_2Cl_2 (10 mL \times 3). The combined organic layer was washed with brine (20 mL), dried over anhydrous MgSO₄, concentrated, and then purified through silica gel column chromatography (1:1, hexanes: CH_2Cl_2 , $R_f = 0.25$) to afford a yellow/green solid. Yield = 136 mg (62%). X-ray quality crystals were obtained from the slow evaporation of a solution of PXZ-IMAC in CH_2Cl_2 /hexanes. mp = 221.2-223.1 °C. ¹H NMR (400 MHz, methylene chloride- $\overline{d_2}$) δ 8.14–8.06 (m, 2H), 7.69 (ddd, J = 18.5, 7.8, 1.4 Hz, 2H), 7.64-7.59 (m, 2H), 7.51-7.36 (m, 2H), 7.34-7.23 (m, 2H), 7.14 (ddd, J = 8.5, 7.4, 1.5 Hz, 1H), 6.83-6.65 (m, 6H), 6.24-6.10 (m, 2H), 1.82 (s, 6H). ¹³C NMR (101 MHz, methylene chloride-d₂) δ 150.36, 144.39, 141.29, 140.98, 136.75, 134.44, 133.71, 133.40, 132.88, 131.95, 131.73, 130.72, 128.43, 126.99, 125.90, 125.01, 123.76, 122.01, 119.12, 117.08, 116.95, 115.85, 113.82, 38.01, 32.98. HRMS (EI) m/z [M^{+•}] calcd for [C₃₄H₂₅N₃O₁]^{+•}, 491.19976; found, 491.19866; difference, -2.24 ppm.

Synthesis of 10-[4-(6,6-Dimethyl-6H-imidazo[4,5,1-de]acridin-1yl)phenyl]-10H-phenothiazine (PTZ-IMAC). A mixture of 5 (100 mg, 0.446 mmol) and 4-(10H-phenothiazin-10-yl)benzaldehyde (149 mg, 0.491 mmol) in EtOH (10 mL) was refluxed for 16 h. The solvent was evaporated under reduced pressure to give a reddish oil, which was redissolved in CH_2Cl_2 (10 mL), followed by the sequential addition of iodine (135 mg, 0.532 mmol) and K₂CO₃ (185 mg, 1.34 mmol). The reaction mixture was stirred at reflux temperature for another 16 h. Upon completion of the reaction, it was quenched with 5% Na₂S₂O₃ (20 mL) and then extracted with CH₂Cl₂ (10 mL \times 3). The combined organic layer was washed with brine (20 mL), dried over anhydrous MgSO₄, concentrated, and then purified through silica gel column chromatography (CH₂Cl₂, $R_f = 0.15$) to afford a yellow solid. Yield = 148 mg (65%). X-ray quality crystals were obtained from the slow evaporation of a solution of PTZ-IMAC in CH₂Cl₂/ hexanes. mp = 259.8-261.1 °C. ¹H NMR (400 MHz, methylene chloride- d_2) δ 8.05–7.97 (m, 2H), 7.70 (dd, J = 7.9, 1.5 Hz, 1H), 7.66 (dd, J = 7.7, 1.1 Hz, 1H), 7.60–7.53 (m, 2H), 7.48–7.38 (m, 2H), 7.35 (dd, J = 8.3, 1.3 Hz, 1H), 7.30–7.20 (m, 3H), 7.12 (tdd, J = 7.8, 6.0, 1.6 Hz, 3H), 7.02 (td, J = 7.5, 1.3 Hz, 2H), 6.74 (dd, J = 8.1, 1.3 Hz, 2H), 1.82 (s, 6H). ¹³C NMR (101 MHz, methylene chloride- d_2) $\delta \ 150.70, \ 144.10, \ 143.82, \ 141.32, \ 136.71, \ 133.83, \ 132.22, \ 131.99,$ 131.22, 130.66, 128.34, 127.84, 127.66, 127.48, 126.97, 125.82, 124.92, 124.28, 123.97, 119.31, 118.96, 117.01, 116.99, 38.00, 32.93.

HRMS (EI) m/z [M^{+•}] calcd for [C₃₄H₂₅N₃S₁]^{+•}, 507.17692; found, 507.17579; difference, -2.22 ppm.

Synthesis of 1-[4-(9,9-Dimethylacridin-10(9H)-yl)phenyl]-6,6-dimethyl-6H-imidazo[4,5,1-de]acridine (ACR-IMAC). A mixture of 5 (100 mg, 0.446 mmol) and 4-(9,9-dimethylacridin-10(9H)-yl)benzaldehyde (154 mg, 0.491 mmol) in EtOH (10 mL) was refluxed for 16 h. The solvent was evaporated under reduced pressure to give a yellow oil, which was redissolved in CH_2Cl_2 (10 mL), followed by the sequential addition of iodine (135 mg, 0.532 mmol) and K₂CO₃ (185 mg, 1.34 mmol). The reaction mixture was stirred at reflux temperature for the 16 h. Upon completion of the reaction, it was quenched with 5% Na₂S₂O₃ (20 mL) and then extracted with CH₂Cl₂ $(10 \text{ mL} \times 3)$. The combined organic layer was washed with brine (20) mL), dried over anhydrous MgSO4, concentrated, and then purified through silica gel column chromatography (CH_2Cl_2 , $R_f = 0.2$) to afford an off white solid. Yield = 144 mg (63%). X-ray quality crystals were obtained from the slow evaporation of a solution of ACR-IMAC in CH_2Cl_2 /hexanes. mp = 246.5-247.6 °C. ¹H NMR (400 MHz, methylene chloride- d_2) δ 8.05–7.92 (m, 2H), 7.55 (ddd, J = 12.9, 7.8, 1.3 Hz, 2H), 7.49–7.43 (m, 2H), 7.40 (dd, J = 7.7, 1.6 Hz, 2H), 7.35-7.19 (m, 3H), 7.13 (td, J = 7.6, 1.3 Hz, 1H), 7.01 (ddd, J = 8.6, 7.3, 1.5 Hz, 1H), 6.95 (ddd, J = 8.3, 7.2, 1.6 Hz, 2H), 6.87 (td, J = 7.4, 1.3 Hz, 2H), 6.36 (dd, J = 8.2, 1.3 Hz, 2H), 1.68 (s, 6H), 1.61 (s, 6H). ¹³C NMR (101 MHz, methylene chloride-*d*₂) δ 150.58, 143.30, 141.35, 141.11, 136.76, 133.78, 133.14, 132.72, 132.22, 131.98, 130.78, 130.71, 128.43, 127.00, 126.82, 125.91, 125.69, 124.99, 121.25, 119.09, 117.11, 117.04, 114.56, 38.03, 36.40, 33.02, 31.32. HRMS (EI) m/z [M^{+•}] calcd for [C₃₇H₃₁N₃]^{+•}, 517.25180; found, 517.25084; difference, -1.86 ppm.

Synthesis of 1-[4-(9H-Carbazol-9-yl)phenyl]-6,6-dimethyl-6Himidazo[4,5,1-de]acridine (CZ-IMAC). A mixture of 5 (100 mg, 0.446 mmol) and 4-(9H-carbazol-9-yl)benzaldehyde (135 mg, 0.498 mmol) in EtOH (10 mL) was refluxed for 16 h. The solvent was evaporated under reduced pressure to give a yellow oil, which was redissolved in CH₂Cl₂ (10 mL), followed by the sequential addition of iodine (135 mg, 0.532 mmol) and K₂CO₃ (185 mg, 1.34 mmol). The reaction mixture was stirred at reflux temperature for the 16 h. Upon completion of the reaction, it was quenched with 5% Na₂S₂O₃ (20 mL) and then extracted with CH_2Cl_2 (10 mL \times 3). The combined organic layer was washed with brine (20 mL), dried over anhydrous MgSO₄, concentrated, and then purified through silica gel column chromatography (1% MeOH in CH_2Cl_2 , $R_f = 0.20$) to afford a light pink solid. The solid was dissolved in a minimal amount of CH₂Cl₂ and layered with hexane to give large X-ray quality crystals of **CZ-IMAC**. Yield = 118 mg (56%). mp = 254.1–255.8 °C. ¹H NMR (400 MHz, DMSO- d_6) δ 8.33 (d, J = 7.8 Hz, 2H), 8.13 (d, J = 8.1 Hz, 2H), 7.93 (d, J = 8.1 Hz, 2H), 7.68-7.59 (m, 3H), 7.59-7.47 (m, 3H), 7.44 (t, J = 7.7 Hz, 1H), 7.38 (t, J = 7.4 Hz, 2H), 7.33–7.19 (m, 3H), 1.77 (s, 6H). ¹³C NMR (101 MHz, DMSO-d₆) δ 149.69, 140.25, 139.85, 138.49, 135.84, 132.69, 131.39, 131.06, 130.78, 130.10, 128.36, 127.03, 126.87, 126.45, 125.67, 124.64, 123.02, 120.64, 120.45, 118.90, 116.40, 116.06, 109.82, 37.28, 32.62. HRMS (EI) m/z [M^{+•}] calcd for [C₃₄H₂₅N₃]^{+•}, 475.20485; found, 475.20331; difference, -3.24 ppm.

Synthesis of 1-[4-(9'H-[9,3':6',9"-tercarbazol]-9'-yl)phenyl]-6,6dimethyl-6H-imidazo[4,5,1-de]acridine (TerCZ-IMAC). A mixture of 5 (58.0 mg, 0.259 mmol) and 4-(9'H-[9,3':6',9"-tercarbazol]-9'yl)benzaldehyde (170 mg, 0.283 mmol) in EtOH (10 mL) and 1,2dichloroethane (10 mL) was refluxed for 16 h. The solvent was evaporated under reduced pressure to give a reddish oil, which was redissolved in 1,2-dichloroethane (10 mL), followed by the sequential addition of iodine (92 mg, 0.36 mmol) and K₂CO₃ (108 mg, 0.781 mmol). The reaction mixture was stirred at reflux temperature for another 16 h. Upon completion of the reaction, it was quenched with 5% Na₂S₂O₃ (20 mL) and then extracted with CH₂Cl₂ (10 mL \times 3). The combined organic layer was washed with brine (20 mL), dried over anhydrous MgSO₄, concentrated, and then purified through silica gel column chromatography (CH₂Cl₂, $R_f = 0.25$) to afford an offwhite solid. Yield = 131 mg (58%). mp = 243.5-245.4 °C. ¹H NMR (400 MHz, methylene chloride- d_2) δ 8.35 (d, J = 2.0 Hz, 2H), 8.23–

8.14 (m, 6H), 8.03–7.97 (m, 2H), 7.88 (d, J = 8.7 Hz, 2H), 7.74–7.63 (m, 4H), 7.49–7.37 (m, 11H), 7.28 (m, 5H), 7.18 (m, 1H), 1.81 (s, 6H) ppm. ¹³C NMR (101 MHz, methylene chloride- d_2) δ 150.55, 142.32, 141.46, 140.97, 139.33, 137.01, 133.97, 132.86, 132.25, 131.24, 130.98, 128.66, 127.78, 127.32, 126.90, 126.51, 126.19, 125.29, 124.91, 123.69, 120.78, 120.32, 120.30, 119.39, 117.29, 117.24, 112.06, 110.29, 38.24, 33.14 ppm. HRMS (EI) m/z [M^{+•}] calcd for [$C_{58}H_{39}N_5$]^{+•}, 805.32055; found, 805.31727; difference, -3.28 ppm.

Synthesis of 9-[4-(6,6-Dimethyl-6H-imidazo[4,5,1-de]acridin-1yl)phenyl]-N³,N³,N⁶,N⁶-tetra(p-tolyl)-9H-carbazole-3,6-diamine (TolCZ-IMAC). A mixture of 5 (74.0 mg, 0.330 mmol) and 4-[3,6bis(di-p-tolylamino)-9H-carbazol-9-yl]benzaldehyde (S3) (300 mg, 0.453 mmol) in EtOH (10 mL) and 1,2-dichloroethane (10 mL) was refluxed for 16 h. The solvent was evaporated under reduced pressure to give a reddish oil, which was redissolved in 1,2-dichloroethane (10 mL), followed by the sequential addition of iodine (117 mg, 0.461 mmol) and K₂CO₃ (137 mg, 0.991 mmol). The reaction mixture was stirred at reflux temperature for another 16 h. Upon completion of the reaction, it was quenched with 5% Na2S2O3 (20 mL) and then extracted with EtOAc (10 mL \times 3). The combined organic layer was washed with brine (20 mL), dried over anhydrous MgSO4, concentrated, and then purified through silica gel column chromatography (1:1, hexanes: CH_2Cl_2 , $R_f = 0.30$) to afford a green solid. Yield = 170 mg (60%). mp = 193.4-195.6 °C. ¹H NMR (400 MHz, benzene-d₆) δ 8.04-7.97 (m, 3H), 7.94-7.88 (m, 2H), 7.48-7.29 (m, 17H), 7.10-6.98 (m, 9H), 2.24 (s, 12H), 1.68 (s, 6H) ppm. ¹³C NMR (101 MHz, benzene- d_6) δ 150.52, 147.05, 142.18, 142.03, 139.41, 138.19, 136.47, 134.12, 132.34, 131.81, 131.65, 131.12, 130.13, 128.38, 128.14, 127.91, 126.79, 126.62, 126.43, 125.47, 125.24, 125.14, 123.26, 118.91, 118.80, 117.92, 117.09, 111.31, 37.76, 32.48, 20.74 ppm. HRMS (EI) m/z [M^{+•}] calcd for [C₆₂H₅₁N₅]^{+•}, 865.41445; found, 865.41440; difference, -0.04 ppm.

9-Benzyl-N³,N³,N⁶,N⁶-tetra(p-tolyl)-9H-carbazole-3,6-diamine (S1). Ditolylamine (11.7 g, 59.0 mmol), 9-benzyl-3,6-diiodo-9Hcarbazole (10.0 g, 19.8 mmol), K2CO3 (21.7 g, 157.0 mmol), Cu powder (5.07 g, 79.7 mmol), and 18-crown-6 (1.04 g, 3.93 mmol) were added to a flame-dried 500 mL round-bottom flask equipped with a magnetic stir bar and reflux condenser. The vessel was evacuated and refilled with N2 three times before addition of dry, degassed o-dichlorobenzene (150 mL). The reaction mixture was heated to reflux and left stirring for 120 h. The reaction mixture was allowed to cool to room temperature, filtered to remove K₂CO₃, and concentrated under reduced pressure. The brown residue was dissolved in CH₂Cl₂ and washed with water three times. The organic layer was collected, dried with MgSO4, filtered and concentrated under reduced pressure. The solid was dissolved in CH2Cl2 and further purified by reprecipitation into hexanes (three times) to afford a yellow powder. Yield = 11.65 g (91%). mp = 132.4-134.2 °C. ¹H NMR (400 MHz, DMSO- d_6) δ 7.81 (d, J = 2.1 Hz, 2H), 7.59 (d, J = 8.8 Hz, 2H), 7.37-7.20 (m, 5H), 7.15 (dd, J = 8.7, 2.2 Hz, 2H), 7.01 (d, J = 8.1 Hz, 8H), 6.91-6.72 (m, 8H), 5.61 (s, 2H), 2.22 (s, 12H).¹³C NMR (101 MHz, DMSO- d_6) δ 145.93, 139.50, 137.76, 130.25, 129.66, 128.63, 127.35, 126.89, 125.44, 122.87, 122.06, 118.32, 110.64, 45.89, 20.24. HRMS (EI) $m/z [M^{+\bullet}]$ calcd for $[C_{47}H_{41}N_3]^{+\bullet}$, 647.33005; found, 667.32831; difference, -2.68 ppm.

 N^3, N^3, N^6, N^6 -Tetra(*p*-tolyl)-9H-carbazole-3,6-diamine (**S2**). AlCl₃ (16.8 g, 126.0 mmol) was suspended in dry, degassed anisole (15 mL) and cooled to 0 °C with stirring. In a separated flask **S1** (11.7 g, 18.0 mmol) was taken up in anisole (50 mL) and then transferred into the AlCl₃ solution, resulting in a color change from yellow to dark brown. Upon heating the reaction to 70 °C the reaction became clear. After 16 h the reaction mixture was poured into water (250 mL) and extracted with toluene (3 × 50 mL). The organic layers were collected, dried over MgSO₄, filtered and concentrated under reduced pressure. The mixture was purified through silica gel column chromatography (hexanes/CH₂Cl₂ 2:1, R_f = 0.25) to afford an off-white solid. Yield = 8.33 g (83%). mp = 258.9–260.8 °C. ¹H NMR (400 MHz, benzene- d_6) δ 7.77 (d, J = 2.1 Hz, 2H), 7.32 (dd, J = 8.6, 2.1 Hz, 2H), 7.16–7.10 (m, 8H), 6.91 (m, 10H), 6.44 (s, 1H), 2.11

(s, 12H). ¹³C NMR (101 MHz, benzene- d_6) δ 147.18, 140.92, 137.50, 130.82, 130.06, 126.24, 124.75, 123.11, 119.19, 111.75, 20.72. HRMS (EI) m/z [M^{+•}] calcd for [C₄₀H₃₅N₃]^{+•}, 557.28310; found, 557.28241; difference, -1.23 ppm.

4-{3,6-Bis[di(p-tolyl)amino]-9H-carbazol-9-yl}benzaldehyde (S3). S2 (500 mg, 0.896 mmol), K₃PO₄ (1.00 g, 4.50 mmol) and DMF (33 mL) were combined in a 100 mL round-bottom flask equipped with a magnetic stir bar and reflux condenser. The reaction was heated to 150 °C before addition of 4-fluorobenzaldehyde (0.30 mL, 2.70 mmol). After stirring for 16 h the reaction mixture was allowed to cool to room temperature, filtered to remove K₃PO₄, and concentrated under reduced pressure. The brown mixture was purified through silica gel column chromatography (hexanes/ CH_2Cl_2 1:1, $R_f = 0.15$) to afford a bright yellow solid. Yield = 340 mg (48%). mp = 141.1–143.0 °C. ¹H NMR (400 MHz, benzene- d_6) δ 9.66 (s, 1H), 7.83 (d, J = 2.1 Hz, 2H), 7.56–7.49 (m, 2H), 7.29 (dd, J = 8.8, 2.1 Hz, 2H), 7.17 (m, 4H), 7.16-7.08 (m, 8H), 6.93 (d, I = 8.2 Hz, 8H), 2.11 (s, 12H). ¹³C NMR (101 MHz, benzene- d_6) δ 189.97, 146.94, 143.01, 142.42, 137.71, 134.96, 131.29, 131.19, 130.16, 126.40, 126.33, 125.46, 123.32, 118.79, 111.13, 20.73. HRMS (EI) m/z [M^{+•}] calcd for [C₄₇H₃₉N₃O]^{+•}, 661.30931; found, 661.30651; difference, -4.24 ppm.

4-(9,9-Dimethyl-10(9H)-acridinyl)benzaldehyde (S4).⁵² To a 3neck, 3 L round-bottom flask was added acridine (26.0 g, 124 mmol), K₃PO₄ (132 g, 621 mmol), and 2.15 L of DMF as well as a magnetic stir bar. A reflux condenser was attached to the flask, then the reaction mixture was heated to reflux. Once refluxing, 4-fluorobenzaldehyde (26.7 mL, 248 mmol) was added to the reaction mixture gradually. The reaction mixture was stirred overnight. After confirmation of the completion of the reaction by TLC, the crude reaction mixture was filtered to remove excess K₃PO₄. The filtrate was then concentrated under reduced pressure then dissolved in 500 mL ethyl acetate. This organic layer was washed three times with 250 mL of deionized water, dried over MgSO₄, filtered and concentrated under reduced pressure. The crude mixture was purified by column chromatography using a gradient of hexane and CH₂Cl₂ (100% hexane to 100% CH₂Cl₂) on silica. Yield = 38.3 g (98%). ¹H NMR (400 MHz, chloroform-d) δ 10.16 (s, 1H), 8.17 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.3 Hz, 2H), 7.55-7.49 (m, 2H), 7.03 (m, 4H), 6.42-6.35 (m, 2H), 1.73 (s, 6H). $^{13}{\rm C}$ NMR (101 MHz, chloroform-d) δ 191.18, 147.47, 140.37, 135.38, 132.20, 131.40, 130.84, 126.45, 125.38, 121.49, 114.87, 36.21, 30.91. HRMS (ESI) m/z [M + H] calcd. for [C₂₂H₁₉NO] + H, 314.1544; found, 314.1545; difference, 0.3 ppm.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.9b02283.

X-ray crystallography details for PXZ-IMAC (CIF) X-ray crystallography details for PTZ-IMAC (CIF) X-ray crystallography details for ACR-IMAC (CIF) X-ray crystallography details for CZ-IMAC (CIF) Synthetic schemes for compounds S1–S4; ¹H and ¹³C{¹H} NMR spectra of all compounds, solvatochromic properties, nanosecond PL decay curves, and cyclic voltammograms of all IMAC compounds (PDF)

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