Synthesis, Characterization, and Structure of Some 1,4-Disubstituted Cyclopenta[d][1,2]oxazines

Nathan C. Tice,[a]* Eric M. Collins,[b] Darrin L. Smith,[c] Chad A. Snyder,[d] Bangbo Yan,[e] and Edwin D. Stevens[e]

[a]Department of Physical Sciences, The University of Findlay, Findlay, Ohio, USA
[b]Department of Chemistry and Biochemistry, Ohio Northern University, Ada, Ohio, USA
[c]Department of Chemistry, Eastern Kentucky University, Richmond, Kentucky, USA
[d]Department of Science and Mathematics, Grace College, Winona Lake, Indiana, USA
[e]Department of Chemistry, Western Kentucky University, Bowling Green, Kentucky, USA
*E-mail: tice@findlay.edu

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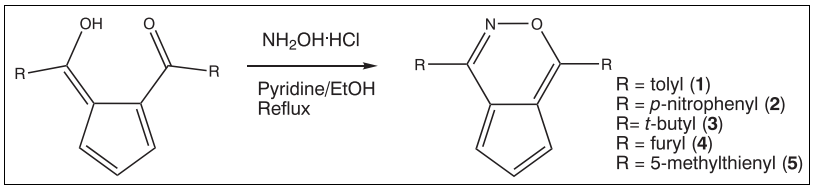

Oxazine-based chemistry offers an alternative to thiophene and pyrrole semiconductors and has been largely unexplored for electronics applications. Discrete monomers or oxazine polymers could serve as an efficient hole carrier for novel devices. A series of 1,4-disubstituted cyclopenta[*d*][1,2]oxazines (R = tolyl, *p*-nitrophenyl, *t*-buytl, furyl, and 5-methylthienyl) were isolated via ring closure with hydroxylamine from a 1,2-acylcyclopentadiene precursor. The target oxazines were characterized by NMR and IR spectroscopy and direct analysis in real time (DART) MS. Single-crystal x-ray structure determination confirmed the identity of the tolyl oxazine, which shows a face-to-face stacking pattern of the heterocyclic rings.

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INTRODUCTION

Heterocycles comprise an important class of organic compounds and offer a wide range of applications that include electronic materials, hydrodesulfurization (HDS) modeling, medicine, and catalysis [1–6]. These compounds have been incorporated into conducting polymers, resulting in semiconducting properties when doped. Of these organic heterocycles, polythiophene and polypyrrole (Fig. 1A, B) and their derivatives are the most common. Both of these polymers offer high synthetic feasibility and processibility [7]. Additionally, polythiophenes have practical advantages over other polymers which include environmental stability and structural versatility [8,9]. Recent applications have included field-effect transistors (FETs), organic light-emitting diodes (OLEDS) [10], and organic photovoltaic (OPV) cells [11].

While thiophenes and pyrroles have been more thoroughly investigated and utilized as next generation materials, oxazines are a similar class of heterocycles that are particularly of interest because of their robust nature and unique structural and electronic properties. Oxazines are six-membered rings that contain both a nitrogen and oxygen atom within the ring itself (Fig. 2). Oxazines that contain aromatic fragments or a fused cyclopentadienyl ring are well known and possess a wide variety of novel medicinal applications [12]. For example, cyclopenta[*d*][1,2] fused-ring oxazines (Fig. 2B) are known for their pharmaceutical effects including inhibitory action towards acetylcholinesterase (anti-Alzheimer) [13], 5-lipoxygenase (anti-Alzheimer) [13], cyclooxygenase 2 (pro-inflammatory disease and anti-diabetic) [14], protein tyrosine phosphatase 1B (insulin resistance) [15], treatment of drug resistant malaria [16], and also to combat certain gram positive bacteria [17]. Some naturally occurring compounds have even been found to incorporate an oxazine ring, especially in marine fungi [18]. Cyclopenta[*d*][1,2]oxazines are also isoelectronic to azulene [19], a well-known topical cream, affording these 5,6-fused rings potentially therapeutic and other pharmacological applications. Similar heterocyclic systems that contain nitrogen and a sulfur heteroatom have also been utilized as voltage-sensitive dyes [20]. Thus, there is a strong potential with oxazines for material applications.

Our primary interest is in the utilization of oxazines and other alternative heterocycles as building blocks for electronic materials that possess novel conducting or optical properties. We have previously reported upon the formation of 5,6-fused pyridazines from a simple 1,2-diacylcyclopentadiene precursor employing hydrazine hydrate [21,22] (Scheme 1, bottom route). This route, initially reported by Linn and Sharkey, also allows for the formation of 5,6-fused oxazines, with ring closure accomplished by hydroxylamine [23] (Scheme 1, top route). Linn and Sharkey only reported oxazines where phenyl and tolyl were employed as the substituents at the

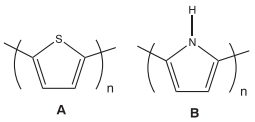


Figure 1. Polythiophene (A) and polypyrrole (B).

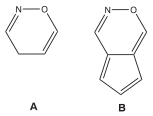
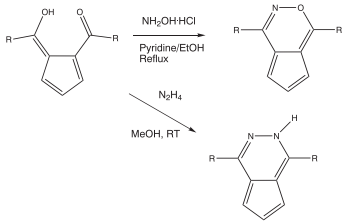


Figure 2. 4H-1,2-oxazine (A) and cyclopenta[d][1,2]oxazine.

Scheme 1. Formation of 1,4-disubstituted cyclopentaoxazines and pyridazines.



1- and 4-position and with limited characterization. Lloyd and Preston utilized a slightly modified version of Linn and Sharkey's route to form the methyl, and *t*-butyl cases, again with limited characterization [19]. There are additional routes towards formation of oxiranes, including for example via [6 + 4] cycloaddition [24]. However, we wished to focus upon the Linn and Sharkey pathway and more fully characterize some of these previously reported oxazines (tolyl and *t*-butyl). Furthermore, we wished to expand this series to other substituent types, including thienyl and furyl cases, to see how general the reaction conditions were. In addition, we also wanted to examine more closely the solid-state nature of these 5,6-fused oxazines and see if their packing properties would be amendable towards device applications. Herein, we report upon the formation, characterization, and solid-state structure of a series of 1,4-disubstituted cyclopenta[*d*][1,2]oxazines.

RESULTS AND DISCUSSION

A series of 1,4-disubstituted cyclopenta[*d*][1,2]oxazines (R = tolyl, *p*-nitrophenyl, *t*-butyl, furyl, and 5-methylthienyl) were isolated and characterized using the procedure initially reported by Linn and Sharkey [23] (Fig. 3).

The 1,2-diacylcyclopentadiene (fulvene) starting materials were synthesized by the reaction of 3 equivalents of lithium cyclopentadianide with 2 equivalents of the appropriate acid chloride. The fulvene precursor was then ring closed by refluxing with hydroxylamine hydrochloride in an anhydrous pyridine/ethanol solution to afford the desired substituted oxazines **1**–**5** in modest yields (28.5–45.8%). These modest yields matched that reported by Linn and Sharkey (44% for the tolyl oxazine **1**). In contrast, the slightly modified Lloyd and Preston procedure employing potassium hydroxide (instead of pyridine as used by Linn and Sharkey) afforded the t-butyl oxazine **3** somewhat higher yield (61%) [19]. Progress of the reaction was monitored via thin-layer chromatography, which afforded different reactions times depending upon the fulvene employed. Increasing reaction time beyond 5 h tended to cause low product yield, presumably due to thermal decomposition. Longer reaction times may have also been necessary because the weaker base pyridine was employed. For each case, upon completion, the reaction mixture was quenched with water, and the oxazines **1**–**5** were isolated as precipitates. Other than the *p*-nitrophenyloxazine **2**, all the target compounds displayed good solubility in common organic solvents (e.g., methylene chloride). Compounds **1**–**5** also displayed reasonably good stability both in air and solution.

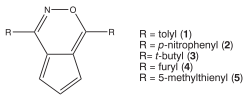
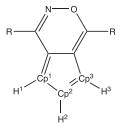


Figure 3. 1,4-Disubstituted cyclopenta[d][1,2]oxazines.

^{1}H NMR spectroscopy confirms the structure for the oxazines **1**–**5** showing both asymmetric Cp and alkyl or aryl substituents (Table 1). The range of chemical shifts (6.5–7.5 ppm) is typical for fused-ring Cp protons [21,22]. Assignment of the of the Cp protons was based upon either coupling observed (triplet for the middle Cp^2 signal) or matching the chemical shift to the proximity of the more electronegative oxygen. However, coupling patterns were complex and difficult to distinguish at times. Even switching solvents from chloroform-*d* to DMSO-*d*^{6} in compound **2** did not resolve the usual coupling behavior, with the Cp signals observed as three doublets. We attribute this complexity to the high degree of electron delocalization and resonance within the Cp moiety. We also observed the disappearance of the characteristic "enolic" signals in the 18–20 ppm range indicative of the fulvene starting material. Cyclopentadianide ring carbons were also observed in ^{13}C NMR spectroscopy, with a narrow range of 115–120 ppm (Table 1). For each of the target compounds, three signals were observed, confirming the asymmetric nature of **1**–**5**. All NMR spectroscopy was carried out in chloroform-*d*, except the p-nitrophenyl

Table 1

Selected ^{1}H and ^{13}C NMR spectroscopic data for products **1**–**5.**



Compound	^{1}H NMR (ppm)			C NMR (ppm)
	H^1	H^2	H^3	Cp^{1-3}
1	6.98 (m)	7.28 (m)	7.39 (m)	115.9 116.7 117.9
2*	7.05 (s)	7.51 (t) J = 1.8 Hz	7.31 (d) J = 4.4 Hz	116.9 118.9 119.5
3	7.19 (d) J = 2.8 Hz	6.98 (t) J = 1.8 Hz	7.19 (d) J = 2.8 Hz	114.5 115.8 116.9
4	6.63 (m)	6.69 (m) J = 2.1 Hz	7.23 (d) J = 3.2 Hz	116.0 116.2 117.7
5	6.90 (d) J = 0.8	6.94 (d) J = 0.8 Hz	7.18 (d) J = 3.2 Hz	115.0 116.2 116.5

^{13}C NMR data obtained in DMSO-d^6.

oxirane **2**. Due to its relatively poor solubility in chloroform, ^{13}C NMR data were obtained in DMSO. Analysis by IR spectroscopy also showed the disappearance of the enolic stretch centered around 3300 cm^{-1} and a set of newly formed N—O stretches at approximately a 1400 and 1600 cm^{-1}. DART mass spectrometry also confirms the molecular mass of oxiranes **1**–**5**, with the expected [M+1]+ ion peak observed for each case. This observance is typical for positive scan mode in DART [25]. Elemental analysis was performed for all previously unreported compounds (oxazines **2**, **4**, and **5**). Both observed hydrogen and nitrogen values matched well with calculated values for **2**, **4**, and **5**. Observed carbon values were slightly higher than calculated values, which we attributed to some thermal sensitivity of these particular oxazines. This correlates well with the decomposition and lower yields observed with extended reaction times. Experimental details and characterization for a representative reaction (Compound **1**) are given in the Experimental section. Full experimental details for all compounds 1–5 are available in the "Supplementary Content."

The identity of the tolyl oxirane **1** was further confirmed by single-crystal X-ray diffraction methods (Fig. 4). Suitable crystals were grown by slow evaporation from methylene chloride in ambient atmosphere and isolated as light yellow plates. Compound **1** crystallized with a triclinic lattice (space group *P*-1), with two molecules in the unit cell. Due to the relatively similar size of the

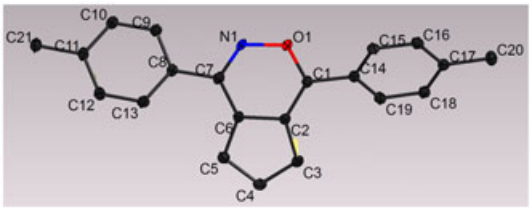


Figure 4. Molecular structure for oxazine 1. [Color figure can be viewed at wileyonlinelibrary.com]

nitrogen and oxygen atom within the oxazine ring (N1 and O1) and near symmetry of the molecule, compound **1** crystallized in two orientations, with the nitrogen oriented viewer-left or viewer-right. This model of the solid-state packing gives a better fit to the X-ray data as compared to the refinement for a single molecular orientation. The major orientation (shown in Fig. 4, with the nitrogen on viewer-left) has a 0.642(8) fractional occupancy (R1 = 4.01% and GoF = 1.041). This model also yields better anisotropic thermal ellipsoids, which failed the rigid bond test in the previous, single orientation model. Data containing the atoms labeled O1B and N1B are the exchanged atom positions in the molecular orientation with the minor occupancy (not shown in the figures here). As expected, the analysis of the structure of **1** shows the presence of a higher degree of double bond character for the N1—C7 bond as compared to O1—C1, with lengths observed at 1.308(3)

and 1.349(2) Å respectively. The carbon–carbon bond lengths had some variation for the Cp ring as well, ranging from 1.3972(10) Å for C3—C4 to 1.4538(9) Å for C2—C6. Bond lengths again were consistent with the expected degree of pi-character based upon the cyclopentadienyl oxazine structure.

The central nine-membered ring (N1, O1, C1—C7) is nearly planar, with the root-mean squared deviation observed at 0.034 Å. Likewise, the puckering parameter (Q) is quite small and correlates with a nearly planar central ring, with an observed value of 0.0832 Å. In the crystal packing, this central ring is pi-stacked with the nine-membered ring of the neighboring molecule related by an inversion center symmetry element (Fig. 5) The Cp portion of one molecule is oriented directly over the oxazine portion of the next molecule. While there are no short contacts (a distance less than the sum of the Van der Waals radii) between these neighboring central rings, there is strong evidence for pi-stacking based upon the distances formed between planes created by the central rings. An inter-planar distance is observed to be 3.375 Å from these adjacent molecules involving the cyclopentadienyl oxazine moiety. This is well within the commonly accepted range for evidence of pi-stacking (3.4–3.6 Å) [26]. In contrast, the tolyl rings are twisted out of the plane of the central ring, with the N1—C7—C8—C9 and O1—C1—C14—C15 torsion angles at 37.8(2)° and 33.3(3)° respectively. The aryl rings do not display any pi-stacking with adjacent moieties. Overall, the pi-stacking observed involving the central ring indicates a strong potential for effective charge transfer in the solid state and potential for these molecules to be utilized as a conducting material.

Tables of crystallographic details, atomic coordinates and displacement parameters, bond distances and angles, intermolecular contact distances, structure factors, and a crystallographic information file (CIF) for the structure of **1** have been deposited with the Cambridge Crystallographic Data Centre [27].

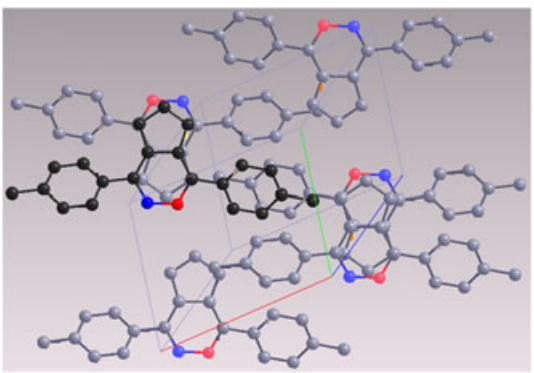


Figure 5. Pi-stacking observed for tolyl oxazine 1. [Color figure can be viewed at wileyonlinelibrary.com]

GENERAL EXPERIMENTAL

All reactions were carried out using standard Schlenk techniques under a nitrogen atmosphere unless otherwise noted. NMR solvent chloroform-*d* (Acros) and DMSO-d^6 (Cambridge Isotope Laboratories), hydroxylamine hydrochloride, magnesium sulfate (Alfa Aesar), anhydrous pyridine, anhydrous ethanol, diethyl ether, pentane, and methylene chloride (Aldrich) were all used without further purification. The 1,2-diacylcyclopentadiene precursors were all made according to previously reported procedures [22,23,28]. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer at ca. 22°C and were referenced to residual solvent peaks and TMS internal standard. All ^{13}C NMR spectra were listed as decoupled. All infrared spectra were recorded on a Perkin Elmer Spectrum One FT-IR Spectrometer. The mass spectrometry analysis was performed with a direct analysis in real-time SVP ion source (IonSense, Saugus, MA, USA) interfaced with a LTQ XL linear ion trap mass spectrometer (Thermo Scientific, San Jose, CA, USA). Specific details for this system and operation have been previously reported [25]. All data reported here are under Positive Scan mode. Melting points were taken on a standard Mel-Temp apparatus.

EXPERIMENTAL

Synthesis of 1,4-di-p-tolylcyclopenta[d][1,2]oxazine (1). In a 25-mL round bottom flask, a solution of 1,2-ditoluylcyclopentadiene (249.7 mg, 0.826 mmol) and hydroxylamine hydrochloride (250.6 mg, 3.606 mmol, 6 mol. eq.) in 5-mL absolute ethanol and 5-mL anhydrous pyridine was refluxed for 2.5 h. The brown solution was quenched with 15-mL distilled water, filtered, and then the precipitate was allowed to dry. The crude product was recrystallized from ethanol to afford 1 as golden yellow solid (113 mg, 45.8% yield). Mp: 170–172°C. Reported: 163–165°C.[23] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 2.47 (s, 3H, Me), 2.49 (s, 3H, Me), 6.98 (m, 1H, Cp), 7.28 (m, 1H, Cp), 7.39 (m, 5H, Cp and Ar), 7.82 (d, 2H, J_3 = 8.0 Hz, Ar), 8.03 (d, 2H, J_3 = 8.0 Hz, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 21.4, 21.6, 115.5, 115.9, 116.7, 117.9 128.6, 129.0, 129.2, 129.4, 129.7, 130.8, 134.3, 140.2, 142.4, 156.2, 165.9 IR (cm^{-1}): 1383, 1612 (strong, N-O), 1800, 1922, 2918. MS(DART-LTQ): m/z 300.33 ([M+1]+). Reported analysis for $C_{21}H_{17}NO$; Calc: C, 84.2; H, 5.7; N, 4.7. Found: C, 84.5; H, 5.8; N, 4.2 [23].

The x-ray crystallographic structure of **1** was determined by single-crystal x-ray structure determination methods. The crystal selected for data collection was typical of others in the batch, which had been grown by slow evaporation from methylene chloride at room temperature.

The crystal was mounted on a MiTeGin microloop with dodecane oil and cooled to 120 K in a stream of cold N_2 gas generated using an Oxford Cryosystems 700 low temperature device. Data were collected at 120 K on a Bruker APEX II Kappa CCD diffractometer. The APEX II software package was used for indexing, data collection and reduction, and for determination of an empirical absorption correction (Bruker APEX II; Bruker AXS Inc.: Madison, WI). The SHELXS/L software package was used for structure solution and refinement [29]. All hydrogen atoms were located in difference Fourier maps and included in the least-squares refinement with isotropic thermal parameters. Refinement with a single orientation of the oxygen and nitrogen atoms in the oxazine ring gave unexpectedly high R-factors and goodness of fit parameters, and unreasonable anisotropic thermal ellipsoids. To improve the fit to the x-ray data, a disordered model was employed in which a second orientation for the oxazine ring was included with the positions of the nitrogen and oxygen atoms interchanged. Bond distance similarity restraints were imposed on the C—N, C—O, and N—O distances in the oxazine rings to ensure a high degree of structural similarity between the two molecular orientations. Crystal data and a summary of experimental details are given in Table 2.

Table 2

Sample and crystal data for Compound 1.

Chemical formula	$C_{21}H_{17}NO$
Formula weight	299.36 g/mol
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal size	0.050 × 0.300 × 0.320 mm
Crystal habit	Light yellow plate
Crystal system	Triclinic
Space group	P − 1
Unit cell dimensions	a = 9.1308 (3) Å α = 105.3736(10)°
	b = 9.8513 (3) Å β = 105.3139(11)°
	c = 9.9497 (3) Å γ = 109.2532(11)°
Volume	751.49(4) $Å^3$
Z	2
Density (calculated)	1.323 g/cm^3
Absorption coefficient	0.081 mm^{-1}
F(000)	316
Theta range for data collection	2.30 to 32.00°
Index ranges	−13 < =h < =9, −14 < =k < =14, −14 < =l < =14
Reflections collected	19701
Independent reflections	5186 [R(int) = 0.0188]
Coverage of independent reflections	98.90%
Absorption correction	Multi-scan
Max. and min. transmission	0.9960 and 0.9750
Refinement method	Full matrix least squares on F^2
Refinement program	SHELXL-2014/7 (Sheldrick, [29])
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data/restraints/parameters	5186/73/295
Goodness-of-fit on F^2	1.048
Δ/σmax	0.003
Final R indices	4855 data; $I > 2\sigma(I)$ R1 = 0.0401, wR2 = 0.1193
	All data; R1 = 0.0419, wR^2 = 0.1213
Weighting scheme	w = 1/ $[\sigma^2(F_o^2) + (0.0783P)^2 + 0.1569P]$ where $P = (F_o^2 + 2F_c^2)/3$
Largest diff. peak and hole	0.492 and −0.301 $eÅ^{-3}$
RMS deviation from mean	0.057 $eÅ^{-3}$

Synthesis of 1,4-di(4-nitrophenyl)cyclopenta[d][1,2]oxazine (2). In a 50-mL round bottom flask, a solution of 1,2-di(4-nitrobenzoyl)cyclopentadiene (163.4 mg, 0.452 mmol) and hydroxylamine hydrochloride (167.1 mg, 2.405 mmol, 8 mol. eq.) in 5 mL absolute ethanol and 5 mL anhydrous pyridine was refluxed for 2 h. The brown solution was quenched with 15-mL distilled water, filtered, and the precipitate was allowed to dry. Product 2 was isolated without further purification as an orange powder (134 mg, 37.4% yield). Mp: 219–223°C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.05 (s, 1H, Cp), 7.31 (d, 1H, J_3 = 4.4 Hz, Cp), 7.51 (t, 1H, J_3 = 1.8 Hz, Cp), 8.12 (d, 2H, J_3 = 8.8 Hz, Ar), 8.31 (d, 2H, J_3 = 8.8 Hz, Ar), 8.46 (d, 2H, J_3 = 8.8 Hz, Ar), 8.48 (d, 2H, J_3 = 8.8 Hz, Ar). ^{1}H NMR (400 MHz, d^6-DMSO, ppm): 7.16 (d, 1H, J_3 = 2.4 Hz, Cp), 7.48 (d, 1H, J_3 = 4.4 Hz, Cp), 7.58 (d, 1H, J_3 = 3.2 Hz, Cp), 8.22 (d, 2H, J_3 = 8.8 Hz, Ar), 8.51 (m, 6H, Ar). ^{13}C NMR (100 MHz, d^6-DMSO, ppm): 114.9, 116.9, 118.9, 119.5, 124.7, 124.9, 130.5, 130.9, 136.7, 137.7, 139.1, 149.3, 149.9, 154.7, 163.0. IR (cm^{-1}): 1348, 1514 (strong, N-O), 1594, 1633 (Ar), 3077. MS(DART-LTQ): m/z 362.17 ([M+1]+). Analysis for $C_{19}H_{11}N_3O_5$; Calc: C, 63.2; H, 3.07; N, 11.63. Found: C, 63.9; H, 3.05; N, 11.48.

Synthesis of 1,4-di-tert-butylcyclopenta[d][1,2]oxazine (3). In a 50-mL round bottom flask, a solution of 1,2-dipivaloylcyclopentadiene (250.2 mg, 1.08 mmol) and hydroxylamine hydrochloride (675 mg, 9.71 mmol, 9 mol. eq.) in 5-mL absolute ethanol and 5-mL anhydrous pyridine was refluxed for 4 h. The yellow solution was quenched with 15-mL distilled water, filtered, and the precipitate was allowed to dry. The crude product was triturated with cold pentane to afford 3 as a light yellow solid (71.0 mg, 28.5% yield). Mp: 71–73°C. Reported: 80–81°C [19]. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.55 (s, 9H, *t*-Bu), 1.62 (s, 9H, *t*-Bu), 6.98 (t, 1H, J_3 = 1.8 Hz, Cp), 7.19 (d, 2H, J_3 = 2.8 Hz, Cp). Reported: (CCl_4) 2.96 (9H, m), 3.18 (9H, m), 8.39 (1H, m), 8.48 (2H, m) [19]. ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 29.0, 29.7, 38.1, 39.3, 113.9, 114.5, 115.8, 116.9, 131.2, 162.6, 177.4. IR (cm^{-1}): 1364, 1600 (N-O). MS(DART-LTQ): m/z 232.17 ([M+1]+). Reported analysis for $C_{15}H_{21}NO$; Calc: C, 77.9; H, 9.15; N, 6.05. Found: C, 78.1; H, 9.4; N, 6.3 [19].

Synthesis of 1,4-di(furan-2-yl)cyclopenta[d][1,2]oxazine (4). In a 50-mL round bottom flask, a solution of 1,2-difuroylcyclopentadiene (249 mg, 0.992 mmol) and hydroxylamine hydrochloride (253 mg, 3.64 mmol, 3.5 mol. eq.) in 5-mL absolute ethanol and 5-mL anhydrous pyridine was refluxed for 3 h. The dark orange solution was quenched with 15-mL distilled water, filtered, and the precipitate was allowed to dry. The crude product was washed with diethyl ether and then triturated with cold pentane to afford 4 as a deep red powder (98 mg, 39.3% yield). Mp: 86–88°C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 6.63 (m, 1H, Cp), 6.69 (m, 1H, Cp), 7.23 (d, 1H, J_3 = 3.2 Hz, Cp), 7.35 (m, 2H, Fur), 7.42 (d, 1H, J_3 = 3.2 Hz, Fur), 7.54 (dd, 1H, J_3 = 0.8 Hz, 4.4 Hz, Fur), 7.72 (s, 1H, Fur), 7.80 (s, 1H, Fur). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 111.8, 111.9, 112.6, 115.7, 116.0, 116.2, 117.7, 134.8, 144.6, 146.8, 146.8, 146.9, 147.6, 154.4. IR (cm^{-1}): 1400, 1627 (strong, N-O), 2200, 3086, 3122. MS(DART-LTQ): m/z 252.08 ([M+1]+). Analysis for $C_{15}H_9NO_3$; Calc: C, 71.7; H, 3.61; N, 5.58. Found: C, 72.3; H, 3.42; N, 5.24.

Synthesis of 1,4-di(5-methylthiophen-2-yl)cyclopenta[d][1,2]oxazine (5). In a 50-mL round bottom flask, a solution of 1,2-di-(5-methylthienoyl)cyclopentadiene (196.4 mg, 0.632 mmol) and hydroxylamine hydrochloride (198.7 mg, 2.86 mmol, 4.4 mol. eq.) in 5-mL absolute ethanol and 5-mL anhydrous pyridine was refluxed for 3 h. The dark orange solution was quenched with 15-mL distilled water, filtered, and the precipitate was allowed to dry. The crude product was washed with diethyl ether and triturated with cold pentane to afford 5 as an orange powder (63.0 mg, 32.1% yield). Mp: 84–86°C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 2.59 (s, 3H, Me), 2.63 (s, 3H, Me) 6.89 (d, 1H, J_3 = 0.8 Hz, Cp), 6.94 (d, 1H, J_3 = 0.8 Hz, Cp), 7.18 (d, 1H, J_3 = 2.8 Hz, Cp), 7.31 (d, 1H, J_3 = 3.2 Hz, Tp), 7.36 (d, 1H, J_3 = 4.4 Hz, Tp), 7.69 (d, 1H, J_3 = 3.6 Hz, Tp), 7.89 (d, 1H, J_3 = 4.0 Hz, Tp). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 115.0, 116.5, 126.1, 127.0, 129.0, 131.8, 133.9, 143.3. IR (cm^{-1}): 1452, 1595 (N-O), 2915, 3073. MS(DART-LTQ): m/z 312.17 ([M+1]+). Analysis for $C_{17}H_{13}NOS_2$; Calc: C, 65.6; H, 4.21; N, 4.50. Found: C, 66.6; H, 4.34; N, 4.21.

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