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Synthesis and characterization of oxadisilole-fused-3,4-dihydro-2*H*-naphtho[2,1-*e*]-1,3-oxazines and 3,4-dihydro-2*H*-anthra[2,1-*e*]-1,3-oxazines

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ABSTRACT

Oxadisilole-fused-3,4-dihydro-2*H*-naphtho[2,1-*e*]-1,3-oxazines and 3,4-dihydro-2*H*-anthra[2,1-*e*]-1,3-oxazines were synthesized through an eco-friendly Mannich type condensation–cyclization reaction of oxadisilole-fused-1-naphthalenol or 1-anthracenol with formaldehyde and primary amines at ambient temperature in high to excellent yields. The photophysical, electrochemical, and thermal properties of these 3,4-dihydro-2*H*-anthra[2,1-*e*]-1,3-oxazine derivatives were also studied.

1. Introduction

The Mannich-type reaction has been widely used[1] as a convenient strategy to prepare a variety of 1,3-oxazine derivatives. It is also an efficient reaction with high atom-economy. Dihydrobenzo/naphtho[*e*]-1,3-oxazines, synthesized from phenols or naphthalenols, formaldehyde, and primary amines via the Mannich reaction, are known to exhibit a wide range of valuable pharmacological properties, such as antitumor,[2] antibacterial,[3] anti-HIV,[4] and antimicrobial agents[5] and antimalarial agents[6] as well as for their versatility as synthetic intermediates.[7] In addition, 6-arylbenzoxazines have been examined as progesterone receptor or modulators and reported as potent nonsteroidal progesterone receptor agonists.[8] Naphthoxazine derivatives have also exhibited therapeutic potential for the treatment of Parkinson's disease.[9] On the other hand, benzoxazines have received considerable attention because the benzoxazine-based polymers derived from ring-opening polymerizations show excellent physical properties, such as high mechanical strength, thermal stability, and durability under a humid environment.[10] These molecules are very useful building blocks for making phenol-type polymers, such as polybenzoxazines, offering lucrative mechanical, and electrical properties.[11] Although several methods for the preparation of dihydrobenzo/naphtho[*e*]-1,3-oxazine derivatives have previously been documented,[5b,c,12] however, dihydroanthra[*e*]-1,3-oxazines have not been reported yet. In this contribution, we report our findings on the synthesis of oxadisilole-fused-3,4-dihydro-2*H*-naphtho[2,1-*e*]-1,3-oxazines **6a**–**g** and 3,4-dihydro-2*H*-anthra[2,1-*e*]-1,3-oxazines **11a**–**f** using oxadisilole-fused-1-naphthalenol **4** or 1-anthracenol **10**, formaldehyde, and primary amines **5a**–**g** as substrates for the Mannich reaction at room temperature. Oxadisilole-fused-1-naphthalenol **4** or 1-anthracenol **10** was synthesized from aromatization of oxabicyclic alkenes **3** or **9**. The oxabicyclic alkenes **3** and **9** are the furan cycloadducts of benzyne **2** and naphthyne **8** generated from benzobis(oxadisilole) **1** and 2,3-naphthoxadisilole **7**, respectively (Schemes 1 and 2).[13] The previously unknown compounds, **11a**–**e** were also characterized, **11b**–**e** show potential as deep-blue emitters for OLED applications because of high fluorescence quantum yields.

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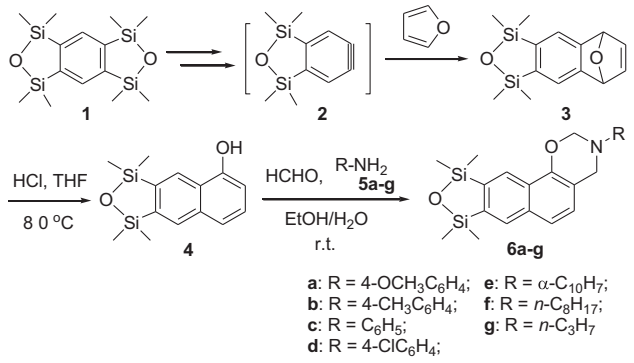
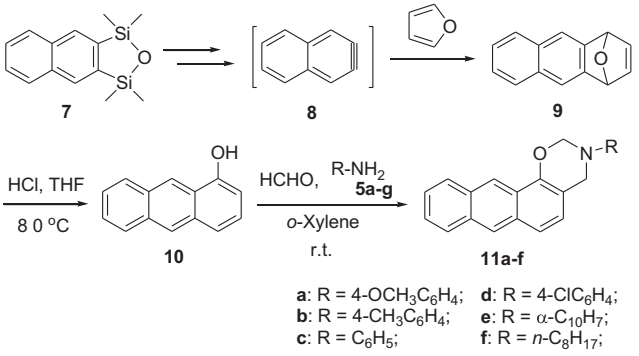


Scheme 1. Synthesis of oxadisilole-fused 3,4-dihydro-2*H*-naphtho[2,1-*e*]-1,3-oxazine derivatives **6a**–**g**.



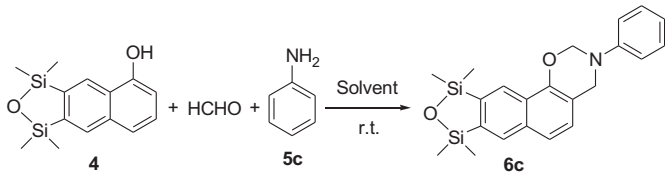
Scheme 2. Synthesis of 3,4-dihydro-2*H*-anthra[2,1-*e*]-1,3-oxazine derivatives **11a**–**f**.

2. Results and discussion

The syntheses of oxadisilole-fused 3,4-dihydro-2*H*-naphtho-[2,1-*e*]-1,3-oxazines **6a**–**g** or 3,4-dihydro-2*H*-anthra[2,1-*e*]-1,3-oxazines **11a**–**f** through an eco-friendly Mannich type condensation–cyclization reaction of oxadisilole-fused 1-naphthalenol **4** or 1-anthracenol **10** with formaldehyde and primary amines **5a**–**g** at room temperature in high to excellent yields are reported. Acidic treatment of oxadisilole-fused benzo-oxabicyclic alkene **3** or naphtho-oxabicyclic alkene **9** in THF at 80 °C gave 92% or 95% yields of oxadisilole-fused-1-naphthalenol **4** or 1-anthracenol **10**, respectively. The oxabicyclic alkene **3** or **9** was prepared in 88% or 54% yield by means of the Diels–Alder cycloaddition of arynes (**2** or **8**) generated from benzobis(oxadisilole) **1** or 2,3-naphthoxadisilole **7** with furan, respectively, via our previously reported phenyliodination/fluoride-induced desilylation protocol (Schemes 1 and 2).[13]

Initially, an one-pot, three components reaction of oxadisilole-fused 1-naphthalenol **4**, formaldehyde, and aniline **5c** (1:2:1) was conducted in water (H_2O) at room temperature for 3 h afforded oxadisilole-fused-3,4-dihydro-2*H*-naphtho[2,1-*e*]-1,3-oxazine **6c** in 73% isolated yield (Scheme 1, Table 1, Entry 1). The effect of various solvents, such as EtOH, EtOH/H_2O (1:1), *o*-xylene, DME, CH_2Cl_2, CH_3CN, and DMF on this reaction was also studied and the results are tabulated in Table 1 (Table 1, Entries 2–8). The use of EtOH/H_2O and *o*-xylene as solvent afforded a higher yield (84% or 86%) of **6c** for 3 h without Lewis acid catalyst (Table 1, Entries 3–4). Certainly, EtOH/H_2O (1:1) is a more environment-friendly solvent for practical use. Varying the reaction time at 1 h, 2 h, 4 h, 6 h or 16 h at room temperature in EtOH/H_2O gave 53–73% yield (Table 1, Entries 9–13). The optimal conditions were obtained when the reaction of oxadisilole-fused 1-naphthalenol **4**, formaldehyde, and aniline **5c** (1:2:1) in EtOH/H_2O (1:1) was carried out at room temperature for 3 h (Table 1, Entry 3).

Table 1
Optimization of the reaction conditions for the synthesis of **6c** from **4**, formaldehyde, and **5c**[a]



Entry	Solvent	Time (h)	Yield[b] of **6c** (%)
1	H_2O	3	73
2	EtOH	3	64
3	EtOH/H_2O (1:1)	3	84
4	*o*-Xylene	3	86
5	DME	3	50
6	CH_2Cl_2	3	80
7	CH_3CN	3	75
8	DMF	3	—
9	EtOH/H_2O (1:1)	1	66
10	EtOH/H_2O (1:1)	2	73
11	EtOH/H_2O (1:1)	4	71
12	EtOH/H_2O (1:1)	6	56
13	EtOH/H_2O (1:1)	16	53

[a] Reaction conditions: 1.5 mmol of **4**, 3.0 mmol of formaldehyde, and 1.5 mmol of **5c**.
[b] Yield of isolated product.

To probe the effect of primary amine on the Mannich reaction of oxadisilole-fused-1-naphthalenol **4** with formaldehyde (Scheme 1), various primary aryl and alkyl amines **5a**–**g** (1:2:1) in EtOH/H_2O (1:1) at room temperature for 3 h were studied. The results are summarized in Table 2 (Entries 1–7). As shown from the results, the Mannich reaction of **4** with formaldehyde is quite susceptible to the electronic nature (X=OCH_3, CH_3, H, Cl) of the substituent on the aryl amines **5a**–**d** (Table 2, Entries 1–4). It was shown that the electron-rich aromatic primary amines afforded a higher yield than the electron-deficient counterparts. The stronger the electron-donating property of the substituent (X=OCH_3) (Table 2, Entry 1), the higher the isolated yield was. In addition, the short aliphatic primary amine **5g** gave a higher yield than the longer counterparts **5f** (Table 2, Entries 6–7). On the other hand, α-naphthylamine, afforded the poor yield (Table 2, Entry 5).

Table 2
Synthesis of **6a**–**g** or **11a**–**f** from **4** or **10**, formaldehyde, and **5a**–**g**[a] via Schemes 1 and 2

Entry	Primary amine	R	Phenol	Product	Yield[b] (%)
1	**5a**	4-$OCH_3C_6H_4$	**4**	**6a**	90
2	**5b**	4-$CH_3C_6H_4$	**4**	**6b**	80
3	**5c**	C_6H_5	**4**	**6c**	84
4	**5d**	4-ClC_6H_4	**4**	**6d**	73
5	**5e**	α-$C_{10}H_7$	**4**	**6e**	55
6	**5f**	*n*-C_8H_{17}	**4**	**6f**	40
7	**5g**	*n*-C_3H_7	**4**	**6g**	76
8	**5a**	4-$OCH_3C_6H_4$	**10**	**11a**	65
9	**5b**	4-$CH_3C_6H_4$	**10**	**11b**	43
10	**5c**	C_6H_5	**10**	**11c**	62
11	**5d**	4-ClC_6H_4	**10**	**11d**	60
12	**5e**	α-$C_{10}H_7$	**10**	**11e**	42
13	**5f**	*n*-C_8H_{17}	**10**	**11f**	62

[a] Reaction conditions: 1.5 mmol of **4** or **10**, 3.0 mmol of formaldehyde, and 1.5 mmol of **5a**–**g**.
[b] Yields of isolated product.

Our attention then turned to use 1-anthracenol **10** as a substrate for the Mannich reactions with formaldehyde and various primary amines **5a**–**f** (1:2:1) at room temperature for 3 h in *o*-xylene. The use of *o*-xylene as a solvent in this three-component Mannich

reaction is due to the poor solubility of 1-anthracenol **10** in EtOH/H_2O (1:1). To our delight, both the electron rich and the electron deficient aryl amines successfully participated in Mannich reaction, affording the desired products of 3,4-dihydro-2*H*-anthra[2,1-*e*]-1,3-oxazine derivatives **11a**–**f** in 42–65% isolated yields (Scheme 2, Table 2, Entries 8–13).

The structures of compounds **6a**–**g** and **11a**–**f** were established by ^1H and ^{13}C NMR spectroscopy, IR spectroscopy, elemental analysis, and high-resolution (HR) MS, which are in good agreement with the expected structures.

The absorption spectra of **11a**–**e** were measured in CH_2Cl_2 and the spectra data are summarized in Table 3. As seen in the absorption spectra shown in Fig. 1, all of **11a**–**e** possess the characteristic of strong β-band absorption at approximately 260 nm for **11a**–**e**, while the long wavelength absorption bands are located between 389 and 390 nm for **11a**–**e**. The substituent effect was also observed for **11a**–**e** in which the electron-withdrawing or electron-donating groups (X=OCH_3, CH_3 or NO_2) result in a slightly red shift in absorption with respect to **11c** (X=H). The photoluminescence spectra of **11a**–**e** in CH_2Cl_2 are shown in Fig. 2, in which they emit in the range of 434–442 as shown in Table 3. A similar substituent effect was also found for the emission maximum for **11a**–**e**, that is, the emission maximum shifts to a longer wavelength for derivatives substituted with an electron-donating or an electron-withdrawing group (i.e., X=OCH_3, CH_3 or NO_2) relative to that of **11c** (X=H), which provides a mean to tune the color emission of this series. The fluorescence quantum yields (Φ) measured in CH_2Cl_2 using norharman as the reference for **11a**–**e** are in the range of 30–68% for the **11b**–**e** (except **11a**). As shown in Table 3, compound **11a**, showed lower fluorescence quantum yield than anthracene (quantum yield is 0.36).[14] This result clearly showed that the Φ_{FL} value dropped sharply with decreasing oxidation potential, and finally reached Φ_{FL}=0.004 in the case where the benzene moiety was 4-dimethoxybenzene (Table 4).[15] Thus, molecules **11b**–**e** show potential as deep-blue emitters for organic light emitting diode (OLED) applications. In addition, the thermal properties of the **11a**–**e** were determined by DSC and TGA analyses with the decomposition temperature in the range of 148–244 °C.

Table 3
Summary of optical measurements and thermal properties of **11a**–**e**

Compd	λ_{max}^{abs} [a] [nm] [ε_{max} $10^3/M^{-1}$ cm^{-1}]	λ_{max}^{em} [a,b] [nm]	Φ_{FL} [c]	T_m [°C]	T_{dec} [d] [°C]
11a	390 (2.05)	442	0.004	119	190
11b	390 (3.19)	436	0.301	142	148
11c	389 (2.87)	434	0.670	225	155
11d	389 (2.55)	434	0.680	245	245
11e	390 (2.64)	436	0.661	244	244

[a] Measured in CH_2Cl_2.
[b] Excited at the absorption maximum.
[c] Using norharman in 0.1 M H_2SO_4 ($\Phi_{330\sim390}$=0.58) as a standard for the **11a**–**e**.
[d] Determined by thermal gravimetric analyzer with a heating rate of 10 °C min^{-1} under N_2.

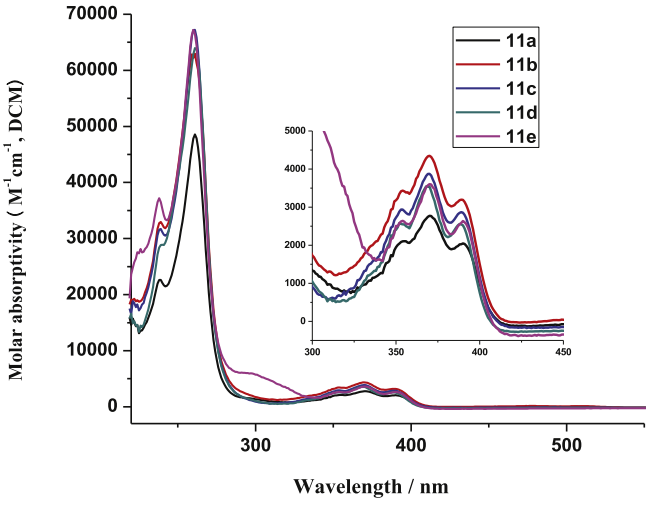


Fig. 1. Absorption spectra of **11a**–**e** in CH_2Cl_2.

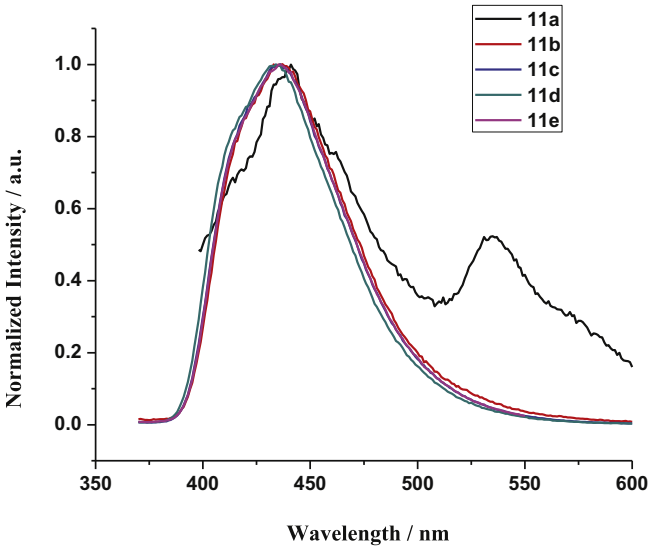


Fig. 2. Emission spectra of **11a**–**e** in CH_2Cl_2.

Table 4
Summary of oxidation potential, HOMO, and LUMO energy levels of **11a**–**e**

Compd	E_{ox} [a], V	HOMO[b], eV	Band gap[c], eV	LUMO[d], eV
11a	0.85	−5.17	3.05	−2.12
11b	0.89	−5.21	3.05	−2.16
11c	0.92	−5.24	3.06	−2.18
11d	0.95	−5.27	3.07	−2.20
11e	0.95	−5.27	3.06	−2.21

[a] E_{ox} estimated by CV method in CH_2Cl_2 using a platinum disk electrode as a working electrode, platinum wire as a counter electrode, and SCE as a reference electrode with an agar salt bridge connecting to compound solution, and ferrocene was used as an external standard, $E_{1/2}$ (Fc/Fc^+)=0.49 V versus SCE and calculated with ferrocene (4.8 eV vs vacuum).
[b] HOMO=E_{ox}−[$E_{1/2}$ (Fc/Fc^+)]+4.8.
[c] Estimated from the absorption edge in CH_2Cl_2.
[d] LUMO=HOMO+Optical band gap.

The redox properties as well as the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energy levels of the **11a**–**e** are tabulated in Table 4. The redox properties of the **11a**–**e** series were studied by cyclic voltammetry, which was carried out in a three-electrode cell setup with 0.1 M of Bu_4NPF_6 as a supporting electrolyte in CH_2Cl_2. All of the potentials reported are referenced to Fc/Fc^+ standard. In contrast to the optical properties, the substituent group on the aryl ring has insignificant effect on the oxidation potential (E_{ox}), which occurs between 0.85 and 0.95 V for **11a**–**e**. The HOMO energy values were calculated according to the equation reported by Schmidt et al. and the LUMO energy level is obtained by subtraction of the optical band gap from the HOMO.[16] Molecules **11a**–**e** show similar HOMO levels. It is also noted that their band gaps are also very similar.

3. Conclusion

Two previously unprecedented oxadisilole-fused-3,4-dihydro-2*H*-naphtho[2,1-*e*]-1,3-oxazines **6a**–**g** or 3,4-dihydro-2*H*-anthra[2,1-*e*]-1,3-oxazines **11a**–**f** derivatives were synthesized through an eco-friendly Mannich type condensation–cyclization reaction of oxadisilole-fused-1-naphthalenol **4** or 1-anthracenol **10** with formaldehyde and primary amines **5a**–**g** under mild conditions. The photophysical, redox, and thermal properties of 3,4-dihydro-2*H*-anthra[2,1-*e*]-1,3-oxazines **11a**–**e** were also characterized. Molecules **11b**–**e** show potential as deep-blue emitters for OLED applications because of high fluorescence quantum yields.

4. Experimental section

4.1. General methods

Purification was conducted on silica gel column chromatography (200–300 mesh silica gel) using mixtures of reagent-grade EtOAc/petroleum ether (PE, 60–80 °C) as the eluents. NMR spectra were recorded at 500 MHz for ^{1}H and 125 MHz for ^{13}C with $CDCl_3$ as the solvent by using a Bruker DRX-500 NMR spectrometer. Chemical shifts are reported in parts per million on the δ scale relative to the residual resonance of $CHCl_3$ (δ=7.26 ppm for ^{1}H, and 77.16 ppm for the central peak of the triplet in ^{13}C). Coupling constants (*J*) are reported in Hertz. IR spectra were recorded with an FTIR spectrometer and expressed in cm^{-1} (KBr disc). Low-resolution mass spectra were obtained with an Agilent spectrometer in EI or API-ES mode and are reported as *m*/*z* values. High-resolution mass spectra were recorded with a Waters Micromass GCT instrument. Element analyses were performed at the Shanghai University. The fluorescence quantum yields in solution were determined by dilution method using norharman ($\Phi_{330\sim390}$=0.58) as a standard. Thermal stabilities were determined by thermal gravimetric analyzer with heating rate of 10 °C min^{-1} under N_2.

*4.1.1. General procedure for the synthesis of 6,7-oxasdisilole-fused-1-naphthalenol (**4**) and 1-anthracenol (**10**).* A mixture of oxabicyclic alkenes **3** or **9** (1 mmol) and 36% concentrated HCl (0.4 mL) in THF (2 mL) was stirred at 85 °C for 4 h. The reaction mixture was cooled to room temperature. Water was added and the resulting mixture was extracted with CH_2Cl_2, The organic extract was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude product, which was further purified by flash chromatography on silica gel using a gradient of 2–5% EtOAc in PE (60–80 °C) as the eluent to afford the compound **4** or **10**.

*4.1.1.1. 6,7-Oxasdisilole-fused-1-naphthalenol (**4**).* Yield: 252 mg, 92%; White solid; mp 188–189 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.459 (6H, s, SiMe), 0.461 (6H, s, SiMe), 5.83 (1H, s, O*H*), 6.85–6.87 (1H, m, Ar–*H*), 7.33–7.36 (1H, t, *J*=8.0 Hz, Ar–H), 7.47 (1H, d, *J*=8.0 Hz, Ar–*H*), 8.06 (1H, s, Ar–*H*), 8.46 (1H, s, Ar–*H*); ^{13}C NMR (125 MHz, $CDCl_3$): δ 1.35, 1.43, 109.3, 121.1, 124.85, 124.91, 126.6, 131.1, 135.0, 143.1, 144.4, 151.9; IR (KBr, cm^{-1}) 3504, 2951, 2895, 1621, 1561, 1449, 1252, 1097; MS (EI): *m*/*z* (%)=274 (37, M^+), 259 (100); HRMS (EI): M^+, found: 274.0845. $C_{14}H_{18}O_2Si_2$ requires 274.0842.

*4.1.1.2. 1-Anthracenol (**10**).* Yield: 184 mg, 95%; White solid; mp 151–152 °C (lit.[16] mp 151–152 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.70 (1H, s, Ar–O*H*), 6.77 (1H, d, *J*=7.0 Hz, Ar–*H*), 7.29–7.32 (1H, m, Ar–*H*), 7.47–7.50 (2H, m, Ar–*H*), 7.63 (1H, d, *J*=8.5 Hz, Ar–*H*), 7.99–8.01 (1H, m, Ar–*H*), 8.05–8.07 (1H, m, Ar–*H*), 8.40 (1H, s, Ar–*H*), 8.80 (1H, s, Ar–*H*); ^{13}C NMR (125 MHz, $CDCl_3$): δ 106.5, 120.8, 121.1, 124.1, 125.3, 125.4, 125.9, 126.1, 128.1, 128.8, 131.4, 132.1, 132.9, 151.5.

*4.1.2. General procedure for the synthesis of the oxasdisilole-fused-3,4-dihydro-2H-naphtho[2,1-e]-1,3-oxazines **6a**–**g**.* The primary amines **5a**–**g** (3.0 mmol) and formalin (37%, w/v, 1.5 mmol) was added by means of a syringe to a stirred mixture of the oxsdisilole-fused-1-naphthalenol **4** (411 mg, 1.5 mmol) in EtOH/H_2O (1:1, 15 mL) at room temperature under N_2 for 3 h. The resulting mixture was extracted with CH_2Cl_2. The organic extract was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude product, which was purified by flash chromatography on silica gel using a gradient of 5–10% EtOAc in PE (60–80 °C) as the eluent to afford the compounds **6a**–**g**.

*4.1.2.1. 3-(4-Methoxyphenyl)-3,4-dihydro-2H-8,9-oxadisilole-fused-naphtho[2,1-e]-1,3-oxazine (**6a**).* Yield: 568 mg, 90%; White solid; mp 175–176 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.43 (6H, s, SiMe), 0.44 (6H, s, SiMe), 3.74 (3H, s, OMe), 4.67 (2H, s, Ar–CH_2–N), 5.48 (2H, s, O–CH_2–N), 6.80 (2H, d, *J*=8.5 Hz, Ar–*H*), 7.12–7.15 (3H, m, Ar–*H*), 7.42 (1H, d, *J*=8.5 Hz, Ar–*H*), 8.00 (1H, s, Ar–*H*), 8.39 (1H, s, Ar–*H*); ^{13}C NMR (125 MHz, $CDCl_3$): δ 1.3, 1.4, 51.3, 55.6, 81.6, 114.6, 115.4, 120.7, 121.4, 124.5, 125.2, 125.4, 131.0, 133.6, 142.7, 143.5, 144.0, 150.0, 155.3; IR (KBr, cm^{-1}) 2958, 2898, 1617, 1565, 1524, 1251, 1094, 841; MS (EI): *m*/*z* (%)=421 (11, M^+), 135 (100); HRMS (EI): M^+, found: 421.1530. $C_{23}H_{27}NO_2Si_3$ requires 421.1532.

*4.1.2.2. 3-(4-Methylphenyl)-3,4-dihydro-2H-8,9-oxadisilole-fused-naphtho[2,1-e]-1,3-oxazine (**6b**).* Yield: 490 mg, 80%; White solid; mp 200–201 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.45 (6H, s, SiMe), 0.46 (6H, s, SiMe), 2.28 (3H, s, Me), 4.72 (2H, s, Ar–CH_2–N), 5.55 (2H, s, O–CH_2–N), 7.06 (2H, d, *J*=9.0 Hz, Ar–*H*), 7.10 (2H, d, *J*=9.0 Hz, Ar–*H*), 7.16 (1H, d, *J*=8.5 Hz, Ar–*H*), 7.43 (1H, d, *J*=8.5 Hz, Ar–*H*), 7.97 (1H, s, Ar–*H*), 8.38 (1H, s, Ar–*H*); ^{13}C NMR (125 MHz, $CDCl_3$): δ 1.3, 1.4, 20.7, 50.8, 80.8, 115.4, 119.2, 120.7, 124.5, 125.2, 125.4, 129.9, 130.9, 131.5, 133.6, 143.4, 144.0, 146.5, 150.0; IR (KBr, cm^{-1}) 2958, 2898, 1617, 1565, 1524, 1251, 1094, 841; MS (EI): *m*/*z* (%)=405 (9, M^+), 57 (100); Anal. Found: C, 67.89; H, 6.62; N, 3.43. $C_{23}H_{27}NO_2Si_2$ requires C, 68.10; H, 6.71; N, 3.45.

*4.1.2.3. 3-Phenyl-3,4-dihydro-2H-8,9-oxadisilole-fused-naphtho[2,1-e]-1,3-oxazine (**6c**).* Yield: 493 mg, 84%; White solid; mp 177–179 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.44 (6H, s, SiMe), 0.45 (6H, s, SiMe), 4.76 (2H, s, Ar–CH_2–N), 5.57 (2H, s, O–CH_2–N), 6.94–6.97 (2H, m, Ar–*H*), 7.16–7.19 (3H, m, Ar–*H*), 7.27–7.30 (2H, m, Ar–*H*), 7.43 (1H, d, *J*=8.0 Hz, Ar–*H*), 8.00 (1H, s, Ar–*H*), 8.40 (1H, s, Ar–*H*); ^{13}C NMR (125 MHz, $CDCl_3$): (125 MHz, $CDCl_3$): δ 1.3, 1.4, 50.6, 80.3, 115.4, 118.8, 120.8, 121.8, 124.4, 125.2, 125.4, 129.4, 131.0, 133.6, 143.5, 144.1, 148.7, 150.0; IR (KBr) 3402, 2923, 1599, 1465, 1442, 1279, 737, 700 cm^{-1}; MS *m*/*z* (%) (EI): 391 (31, M^+), 271 (100); Anal. Found: C, 67.11; H, 6.56; N, 3.61. $C_{22}H_{25}NO_2Si_2$ requires C, 67.47; H, 6.43; N, 3.58.

*4.1.2.4. 3-(4-Chlorophenyl)-3,4-dihydro-2H-8,9-oxadisilole-fused-naphtho[2,1-e]-1,3-oxazine (**6d**).* Yield: 467 mg, 73%; White solid; mp 195–196 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.46 (6H, s, SiMe), 0.47 (6H, s, SiMe), 4.71 (2H, s, Ar–CH_2–N), 5.52 (2H, s, O–CH_2–N), 7.10 (2H, d, *J*=9.0 Hz, Ar–*H*), 7.15 (1H, d, *J*=8.0 Hz, Ar–*H*), 7.22 (2H, d, *J*=9.0 Hz, Ar–*H*), 7.46 (1H, d, *J*=8.0 Hz, Ar–*H*), 8.02 (1H, s, Ar–*H*), 8.41 (1H, s, Ar–*H*); ^{13}C NMR (125 MHz, $CDCl_3$): δ 1.3, 1.4, 50.8, 80.1, 115.0, 120.0, 121.0, 124.4, 125.0, 125.3, 126.8, 129.3, 131.0, 133.6, 143.7, 144.3, 147.4, 149.9; IR (KBr, cm^{-1}) 2955, 2871, 1597, 1564, 1502, 1253, 1096, 841; MS (EI): *m*/*z* (%)=426 (5, M^+), 271 (100); Anal. Found: C, 61.98; H, 5.60; N, 3.35. $C_{22}H_{24}ClNO_2Si_2$ requires C, 62.02; H, 5.68; N, 3.29.

*4.1.2.5. 3-(α-Naphthyl)-3,4-dihydro-2H-8,9-oxadisilole-fused-naphtho[2,1-e]-1,3-oxazine (**6e**).* Yield: 364 mg, 55%; Yellow solid; mp 197–199 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.47 (6H, s, SiMe),

0.48 (6H, s, SiMe), 4.82 (2H, s, Ar–CH_2–N), 5.62 (2H, s, O–CH_2–N), 7.11 (1H, d, J=8.5 Hz, Ar–H), 7.28–7.31 (1H, m, Ar–H), 7.43–7.47 (2H, m, Ar–H), 7.52–7.56 (1H, m, Ar–H), 7.59–7.62 (2H, m, Ar–H), 7.87 (1H, d, J=8.0 Hz, Ar–H), 8.04 (1H, s, Ar–H), 8.30 (1H, d, J=8.5 Hz, Ar–H), 8.49 (1H, s, Ar–H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 1.3, 1.4, 52.3, 82.2, 115.5, 118.0, 120.8, 123.6, 124.6, 124.8, 125.3, 125.5, 126.01, 126.04, 126.1, 128.7, 129.1, 131.0, 133.7, 134.9, 143.6, 144.1, 146.2, 149.6; IR (KBr, cm^{-1}) 2955, 2897, 1626, 1560, 1464, 1252, 1096, 839; MS (EI): m/z (%)=441 (10, M^+), 57 (100); Anal. Found: C, 70.48; H, 6.23; N, 3.14. $C_{24}H_{37}NO_2Si_2$ requires C, 70.70; H, 6.16; N, 3.17.

*4.1.2.6. 3-Octyl-3,4-dihydro-2H-8,9-oxadisilole-fused-naphtho-[2,1-e]-1,3-oxazine (**6f**).* Yield: 256 mg, 40%; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.55 (6H, s, SiMe), 0.56 (6H, s, SiMe), 1.00 (3H, t, J=7.0 Hz, CH_2–CH_3), 1.39–1.42 (12H, m, CH_2), 2.90 (2H, t, J=7.0 Hz, N–CH_2–CH_2), 4.19 (2H, s, Ar–CH_2–N), 5.16 (2H, s, O–CH_2–N), 7.15 (2H, d, J=8.5 Hz, Ar–H), 7.47 (1H, d, J=8.5 Hz, Ar–H), 8.10 (1H, s, Ar–H), 8.55 (1H, s, Ar–H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 1.3, 1.4, 14.2, 22.7, 27.4, 28.3, 29.4, 29.6, 31.9, 50.5, 51.8, 83.0, 114.6, 120.2, 124.4, 125.1, 126.0, 130.9, 133.6, 143.2, 143.7, 149.6; IR (KBr, cm^{-1}) 2955, 2927, 1626, 1562, 1425, 1252, 1096, 841; MS (EI): m/z (%) 427 (1, M^+), 273 (100); HRMS (EI): M^+, found: 427.2363. $C_{24}H_{37}NO_2Si_2$ requires 427.2361.

*4.1.2.7. 3-Propyl-3,4-dihydro-2H-8,9-oxadisilole-fused naphtha-[2,1-e]-1,3-oxazine (**6g**).* Yield: 407 mg, 76%; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.50 (6H, s, SiMe), 0.51 (6H, s, SiMe), 1.00 (3H, t, J=7.0 Hz, CH_2–CH_3), 1.67–1.71 (2H, m, CH_2–CH_3), 2.83 (2H, t, J=7.0 Hz, N–CH_2–CH_2), 4.16 (2H, s, Ar–CH_2–N), 5.13 (2H, s, O–CH_2–N), 7.12 (1H, d, J=8.0 Hz, Ar–H), 7.43 (1H, d, J=8.0 Hz, Ar–H), 8.05 (1H, s, Ar–H), 8.47 (1H, s, Ar–H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 1.3, 1.4, 11.8, 21.5, 50.5, 53.8, 83.1, 114.7, 120.2, 124.4, 125.1, 126.1, 131.0, 133.6, 143.2; IR (KBr, cm^{-1}) 2962, 2903, 1626, 1562, 1470, 1250, 1098, 841; MS(EI): m/z (%) 357 (22, M^+), 271 (100); HRMS (EI): M^+, found: 357.1580. $C_{19}H_{27}NSi_2O_2$ requires 357.1579.

*4.1.3. General procedure for the synthesis of the 3,4-dihydro-2H-anthra[2,1-e]-1,3-oxazines **11a**–**f**.* The primary amines **5a**–**f** (3.0 mmol) and formalin (37%, w/v, 1.5 mmol) was added by means of a syringe to a stirred mixture of the 1-anthracenol **10** (291 mg, 1.5 mmol) in *o*-xylene (15 mL) at room temperature under N_2 for 3 h. The resulting mixture was extracted with CH_2Cl_2, The organic extract was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude product, which was purified by flash chromatography on silica gel using a gradient of 5–10% EtOAc in PE (60–80 °C) as the eluent to afford the compounds **11a**–**f**.

*4.1.3.1. 3-(4-Methoxyphenyl)-3,4-dihydro-2H-anthra[2,1-e]-1,3-oxazine (**11a**).* Yield: 333 mg, 65%; Yellow solid; mp 118–120 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.73 (3H, s, OMe), 4.67 (2H, s, Ar–CH_2–N), 5.53 (2H, s, O–CH_2–N), 6.81 (2H, d, J=9.0 Hz, Ar–H), 7.08 (1H, d, J=8.5 Hz, Ar–H), 7.16–7.17 (2H, m, Ar–H), 7.44–7.48 (2H, m, Ar–H), 7.56 (2H, d, J=8.5 Hz, Ar–H), 7.96–8.03 (2H, m, Ar–H), 8.33 (1H, s, Ar–H), 8.72 (1H, s, Ar–H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 51.6, 55.6, 81.4, 112.8, 114.6, 120.3, 120.7, 121.2, 124.5, 125.4, 125.6, 126.0, 128.1, 128.8, 131.5, 131.7, 131.9, 142.8, 149.5, 155.2; IR (KBr, cm^{-1}) 2948, 2833, 1640, 1513, 1465, 1252, 1071, 845; MS (EI): m/z (%)=341 (1, M^+), 120 (100); HRMS (EI): M^+, found: 341.1416. $C_{23}H_{19}NO_2$ requires 341.1415.

*4.1.3.2. 3-(4-Methylphenyl)-3,4-dihydro-2H-anthra[2,1-e]-1,3-oxazine (**11b**).* Yield: 210 mg, 43%; Yellow solid; mp 141–142 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.29 (3H, s, Me), 4.72 (2H, s, Ar–CH_2–N), 5.60 (2H, s, O–CH_2–N), 7.09–7.16 (5H, m, Ar–H), 7.47–7.49 (2H, m, Ar–H), 7.57 (1H, d, J=8.5 Hz, Ar–H), 7.98–8.00 (1H, m, Ar–H), 8.05–8.07 (1H, m, Ar–H), 8.34 (1H, s, Ar–H), 8.76 (1H, s, Ar–H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.7, 51.0, 80.6, 112.8, 119.0, 120.3, 120.7, 124.4, 124.5, 125.4, 125.6, 126.0, 128.1, 128.8, 129.9, 131.3, 131.5, 131.6, 131.8, 146.6, 149.5; IR (KBr, cm^{-1}) 2916, 2856, 1640, 1620, 1519, 1267, 1070, 843; MS (EI): m/z (%)=325 (21, M^+), 206 (100); HRMS (EI): M^+, found: 325.1467. $C_{23}H_{19}NO$ requires 325.1464.

*4.1.3.3. 3-Phenyl-3,4-dihydro-2H-anthra[2,1-e]-1,3-oxazine (**11c**).* Yield: 289 mg, 62%; Yellow solid; mp 224–226 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.75 (2H, s, Ar–CH_2–N), 5.62 (2H, s, O–CH_2–N), 6.96–6.99 (1H, m, Ar–H), 7.10 (1H, d, J=8.5, Ar–H), 7.23–7.25 (2H, m, Ar–H), 7.30–7.33 (2H, m, Ar–H), 7.48–7.50 (2H, m, Ar–H), 7.57 (1H, d, J=8.5 Hz, Ar–H), 7.98–8.00 (1H, m, Ar–H), 8.05–8.07 (1H, m, Ar–H), 8.34 (1H, s, Ar–H), 8.76 (1H, s, Ar–H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 50.8, 80.0, 112.8, 118.5, 120.2, 120.8, 121.7, 124.4, 124.5, 125.4, 125.6, 126.0, 128.1, 128.8, 129.4, 131.5, 131.6, 131.9, 148.8, 149.6; IR (KBr, cm^{-1}) 2880, 2786, 1640, 1596, 1553, 1269, 1069, 838; MS (EI): m/z (%)=311 (18, M^+), 206 (100); HRMS (EI): M^+, found: 311.1310. $C_{22}H_{17}NO$: 311.1313.

*4.1.3.4. 3-(4-Chlorophenyl)-3,4-dihydro-2H-anthra[2,1-e]-1,3-oxazine (**11d**).* Yield: 311 mg, 60%; Yellow solid; mp 235–236 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.69 (2H, s, Ar–CH_2–N), 5.55 (2H, s, O–CH_2–N), 7.06–7.14 (3H, m, Ar–H), 7.21–7.24 (2H, m, Ar–H), 7.45–7.49 (2H, m, Ar–H), 7.57 (1H, d, J=8.5 Hz, Ar–H), 7.97–8.04 (2H, m, Ar–H), 8.33 (1H, s, Ar–H), 8.71 (1H, s, Ar–H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 51.0, 79.9, 112.5, 119.9, 120.2, 121.0, 124.2, 124.4, 125.6, 125.8, 126.1, 126.7, 128.1, 128.8, 129.3, 131.55, 131.61, 131.9, 147.5, 149.5; IR (KBr, cm^{-1}) 2939, 2884, 1631, 1592, 1575, 1264, 1068, 842; MS (EI): m/z (%)=345 (11, M^+), 206 (100); HRMS (EI): M^+, found: 345.0920. $C_{22}H_{16}ClNO$ requires 345.0922.

*4.1.3.5. 3-(α-Naphthdyl)-3,4-dihydro-2H-anthra[2,1-e]-1,3-oxazine (**11e**).* Yield: 227 mg, 42%; Yellow solid; mp 178–180 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.78 (2H, s, Ar–CH_2–N), 5.66 (2H, s, O–CH_2–N), 7.04 (1H, d, J=9.0 Hz, Ar–H), 7.28–7.31 (1H, m, Ar–H), 7.47–7.62 (7H, m, Ar–H), 7.87 (1H, d, J=8.5 Hz, Ar–H), 7.98–8.07 (2H, m, Ar–H), 8.32 (1H, J=8.5 Hz, Ar–H), 8.35 (1H, s, Ar–H), 8.80 (1H, s, Ar–H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 52.4, 82.2, 112.9, 117.7, 120.3, 120.8, 123.7, 124.5, 124.8, 125.5, 125.7, 126.02, 126.04, 126.1, 128.1, 128.7, 128.8, 129.1, 131.6, 131.7, 131.9, 134.9, 146.3, 149.1; IR (KBr, cm^{-1}) 2939, 2884, 1631, 1592, 1575, 1264, 1068, 842; MS (EI): m/z (%)=361 (2, M^+), 154 (100); HRMS (EI): M^+, found: 361.1467. $C_{26}H_{19}NO$ requires 361.1470.

*4.1.3.6. 3-(Octyl)-3,4-dihydro-2H-anthra[2,1-e]-1,3-oxazine (**11f**).* Yield: 323 mg, 62%; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.92 (3H, t, J=7.0 Hz, CH_2–CH_3), 1.30–1.35 (12H, m, CH_2), 2.86 (2H, t, J=7.0 Hz, N–CH_2–CH_2), 4.13 (2H, s, Ar–CH_2–N), 5.14 (2H, s, O–CH_2–N), 7.06 (1H, d, J=9.0, Ar–H), 7.46–7.48 (2H, m, Ar–H), 7.55 (1H, d, J=8.5, Ar–H), 7.98–8.07 (2H, m, Ar–H), 8.34 (1H, s, Ar–H), 8.74 (1H, s, Ar–H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.2, 22.8, 27.4, 28.5, 29.4, 29.7, 32.0, 50.6, 52.1, 83.1, 112.1, 120.1, 120.2, 124.3, 125.31, 125.33, 125.5, 126.0, 128.1, 128.8, 131.5, 131.7, 131.8, 149.1; IR (KBr, cm^{-1}) 2926, 2853, 1632, 1571, 1556, 1262, 1079, 910, 720; MS (EI): m/z (%)=347 (2, M^+), 84 (100); HRMS (EI): M^+, found: 347.2249. $C_{24}H_{29}NO$ requires 347.2254.

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