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Longer-Wavelength-Absorbing, Extended Chalcogenorhodamine Dyes

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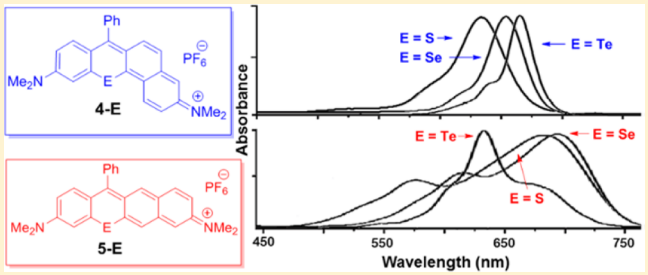
Supporting Information

ABSTRACT: Extended rhodamines were prepared by inserting an additional fused benzene ring into the rhodamine xanthylium core. The synthesis of "bent" dyes **4-E** (E = S, Se, Te) began with regioselective lithiation of the 1-position of *N*,*N*-diisopropyl 6-dimethylamino-2-naphthamide (**11b**) with *n*-BuLi/TMEDA (≥25:1 1- vs 3-lithiation) followed by addition of a dichalcogenide electrophile. The synthesis of "linear" dyes **5-E** (E = S, Se, Te) began with regioselective lithiation of the 3-position of *N*,*N*-diethyl 6-dimethylamino-2-naphthamide (**11a**) with lithium tetramethylpiperidide (≥50:1 3- vs 1-lithiation) followed by addition of a dichalcogenide electrophile. Dyes **4-E** and **5-E** have absorption maxima in the 633−700 nm range. Dyes **4-E** generate singlet oxygen upon irradiation while dyes **4-S** and **5-S** are highly fluorescent, with quantum yields for fluorescence of 0.47 and 0.18, respectively. DFT calculations were performed on the **4-E** and **5-E** chromophores. For the dyes **4-E**, the lowest energy excitation is due solely to the HOMO−LUMO transition. For dyes **5-E**, the lowest energy excitation is a combination of two excitations, both having contributions from the HOMO to LUMO and HOMO-1 to LUMO.



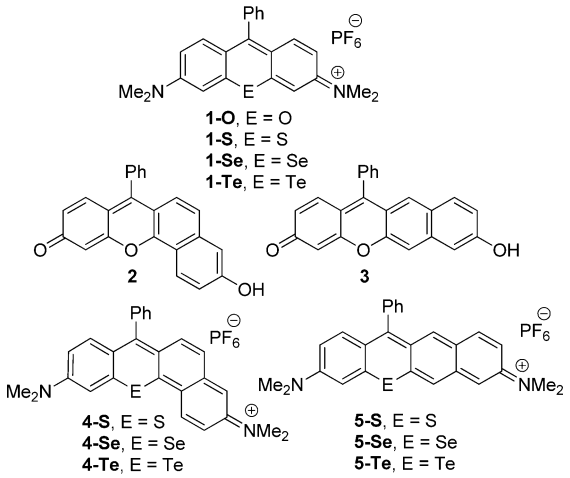
INTRODUCTION

The cationic rhodamine dyes such as tetramethylrosamine (**1-O**, Chart 1) are based on the xanthylium nucleus. The rhodamines are important chromophores in chemistry and biology and are used as laser dyes, fluorescent labels, and fluorescence emission standards where their high fluorescence quantum yields and photostabilities are exploited.[1−10] The 500−550 nm window for absorption maxima in the rhodamines is one of their limitations since it is outside the 600−900 nm window of maximum transparency in biological tissue. Heavy chalcogen analogues of the rhodamines (**1-S**, **1-Se**, and **1-Te**, Chart 1) absorb in the 570−600 nm window with the tellurorhodamines having the longest wavelength absorption maxima.[11,12] More recently, chalcogenorhodamines with additional fused rings to restrict rotation of the 3- and 6-amino substituents in the xanthylium core extend absorption maxima to 630 nm.[13−15] The longer wavelength-absorbing seleno- and tellurorhodamines are also effective photosensitizers for the generation of singlet oxygen,[11,14,15] the generation of photocurrents,[16−18] and for the photochemical reduction of protons to hydrogen.[19]

Another approach to longer-wavelength-absorbing xanthene dyes focused on the extension of the chromophore through additional fused benzene rings.[7a,20,21] Compounds **2** and **3** (Chart 1) are representative examples of extended fluorescein-related molecules with longer wavelengths of absorption and emission. Chalcogenorhodamine-related structures with similar additional fused rings should absorb and emit at longer wavelengths than their xanthylium-based analogues.

Herein, the syntheses of extended chalcogenorhodamine chromophores are described utilizing the regioselective metalation of 6-dimethylamino-2-naphthamides at the 1-position for the preparation of dyes **4-E** (Chart 1) and the 3-position for the

Chart 1. Structures of the Chalcogenorosamines 1-E, Extended Fluoresceins 2 and 3, and Extended Chalcogenorhodamines 4-E and 5-E



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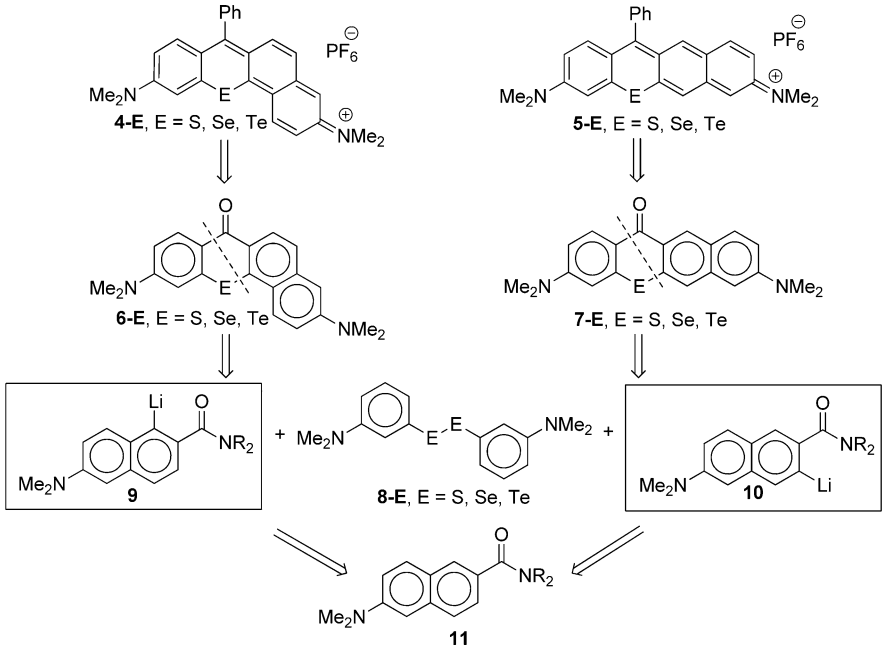
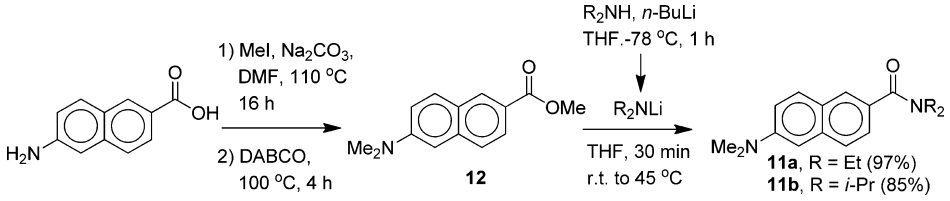
Scheme 1. Retrosynthetic Analysis of Extended Rhodamines 4-E and 5-E from 6-Dimethylamino-2 Naphthamide Derivatives 11



Scheme 2. Synthesis of 6-Dimethylamino-2-naphthamide Derivatives 11



preparation of dyes **5-E**. The photophysical properties of **4-E** and **5-E** are compared to those of the parent rhodamine **1-O** and the heavier chalcogen analogues **1-S**, **1-Se**, and **1-Te** (Chart 1). The extended conjugation in **4-E** and **5-E** increases the absorption maxima (λ_{max}) to wavelengths >640 nm. The extended chalcogenorhodamine chromophores were also examined computationally using density functional theory (DFT).

RESULTS AND DISCUSSION

Synthesis of Extended Rhodamine Dyes 4-E and 5-E. The approach to extended rhodamine dyes **4-E** and **5-E** is shown in the retrosynthetic analysis of Scheme 1. Addition of an aryl Grignard reagent to the appropriate extended xanthone **6-E** or **7-E** followed by an acidic workup would give the cationic extended rhodamine. The extended xanthones **6-E** and **7-E** can be prepared via addition of dichalcogenides **8-E** to 1-lithio-6-dimethylamino-2-naphthamide **9** or 3-lithio-6-dimethylamino-2-naphthamide **10**, respectively, followed by cyclization of the resulting amide derivatives. The selective lithiation of a 6-dimethylamino-2-naphthamide **11** to deliver **9** or **10** is key to the synthetic plan.

Synthesis of 6-dimethylamino-2-naphthamide derivatives **11** began with methylation of 6-amino-2-naphthoic acid with iodomethane and sodium carbonate in DMF at 110 °C (Scheme 2). Formation of methyl 6-dimethylamino-2-naphthoate **12** was accompanied by formation of some of the 6-trimethylammonium derivative from over alkylation. The quaternary trimethylammonium salt was demethylated via the addition of 1,4-diazabicyclo[2.2.2]octane (DABCO). Overall, naphthoate **12** was isolated in 99% yield. Ester **12** was converted to amides **11** via the addition of lithium diethylamide to give **11a** in 97% yield or lithium diisopropylamide to give **11b** in 85% yield as shown in Scheme 2.

In our synthetic approach to the **1-E** derivatives and to other chalcogenorhodamines, directed metalations of 4-dimethylamino-substituted benzamide derivatives with *s*-BuLi/TMEDA or *t*-BuLi/TMEDA gave 2-lithio-4-dimethylaminobenzamides in excellent yield, which then reacted with dichalcogenides **8-E** to give the xanthone precursors.[22] A similar approach with naphthamides **11** should lead to precursors to xanthones **6-E** from 1-lithio-2-naphthamides **9** and to **7-E** from 3-lithio-2-naphthamides **10**. However, the regiochemical preference for metalation with *t*-BuLi or *s*-BuLi/TMEDA to give **9** and/or **10** is not clear.

The regioselectivity of directed metalation of 2-substituted naphthalenes varies with the specific substrate, directing group, base, and solvent conditions.[23−27] The regioselective synthesis of 2,3-di- and 1,2,3-trisubstituted naphthalenes via a directed metalation strategy with *N*,*N*-diethyl-*O*-naphthyl-2-carbamates has been recently reported.[28] However, studies of the regioselectivity of directed ortho-metalation of naphthyl-2-amides has been limited and has given poor selectivity as shown in Scheme 3.[23] The directed ortho-metalation of *N*,*N*-diisopropyl 2-naphthamide with *s*-BuLi/TMEDA at −78 °C in THF followed by reaction with DMF gave 1,2- and 2,3-disubstituted naphthalenes **13** and **14** in 22% and 10% isolated yields, respectively.[23] Bulky bases or bulky amide groups have

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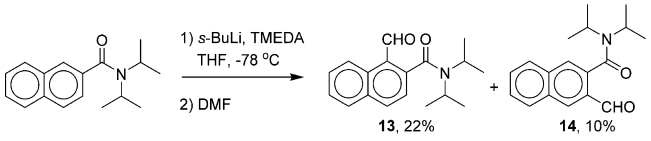
Organometallics XXXX, XXX, XXX−XXX

Scheme 3. Directed Metalations of 2-Naphthamide Derivatives from Reference 23



allowed selective metalation at the 1-position but not the 3-position. Directed metalation of *N,N*-diethyl 6-methoxy-2-naphthamide with *t*-BuLi at −78 °C in THF and quenching with iodoethane gave *N,N*-diethyl 6-methoxy-1-ethyl-2-naphthamide, the product of metalation at the 1-position, in 68% yield.[28] Similarly, directed metalation of *N,N*-diisopropyl 6-methoxy-2-naphthamide with *n*-BuLi at −78 °C in THF followed by reaction quenching with iodoethane gave *N,N*-diisopropyl 6-methoxy-1-ethyl-2-naphthamide in 95% isolated yield, again, from metalation at the 1-position.[28] With the diisopropylamide, nucleophilic addition of *n*-BuLi was not observed.

Amide **11a** was subjected to directed metalation with *s*-BuLi and TMEDA at −78 °C, and the resulting mixture of anions was quenched with dichalcogenides **8-E** (Scheme 4). Inseparable mixtures of **15-E**/**16-E** were isolated. Lithiation at the 1-position was favored by a ratio of 2.5:1 to 3.3:1 as determined by ^{1}H NMR spectroscopy (Supporting Information) as shown in Table 1, entries 1−3. The structures of **15-E** and **16-E** were assigned unambiguously by cyclization of the mixtures with $POCl_3/Et_3N$[29] to give extended chalcogenoxanthones **6-E** and **7-E** in a ratio of 2.5:1 to 3.3:1 (Scheme 4). The chalcogenoxanthones **6-E** and **7-E** were separable by chromatography on SiO_2.

The reaction of *t*-BuLi with **11a** at −78 °C followed by addition of diselenide **8-Se** gave a 3:1 mixture of 1-substituted **15-Se** and 3-substituted **16-Se**, respectively (Table 1, entry 4). Although the lithiation of the 1-position was favored, the bulkier *t*-BuLi did not give improved regioselectivity. We also examined the directed metalation of **11a** with *n*-BuLi/TMEDA followed by the addition of **8-Se**. Ketones **17** and **18** were isolated from the product mixture in 40% and 30% yields, respectively (Table 1, entry 5). Ketone **17** formed as a result of nucleophilic addition of *n*-BuLi to the diethylamide moiety, while the ketone **18** resulted from enolate formation from ketone **17** and subsequent attack by the electrophile **8-Se**.

The impact of increasing the steric bulk of the amide alkyl groups in *N,N*-diisopropyl naphthamide **11b** on regioselectivity was next examined. Directed metalation of **11b** with *s*-BuLi and TMEDA at −78 °C followed by quenching with disulfide **8-S** gave an inseparable 2.5:1 mixture of **19-S**/**20-S** (Table 1, entry 6). Directed metalation of **11b** with *n*-BuLi/TMEDA followed by the addition of the dichalcogenides **8-E** (Scheme 5) gave the 1,2-disubstituted products **19-E** as the major products in these reactions with the 2,3-disubstituted regioisomers **20-E** present at ≤4% by ^{1}H NMR spectroscopy (Table 1, entries 7−9). Steric interactions between the isopropyl protons on the amides with the peri 8-hydrogen on the naphthamide ring (inset of Scheme 5) would serve to shield the 3-proton from deprotonation while allowing approach of the base to the 1-proton. The dichalcogenide electrophile **8-E** had minimal impact on the reaction as shown in the specific products of Scheme 5: sulfide **19-S** was isolated in 80% yield, selenide **19-Se** was isolated in 82% yield, and telluride **19-Te** was isolated in 94% yield.

The preferential lithiation of the 3-position of naphthamide **11a** was approached using bulky lithium amide bases. Our reasoning was that bulky dialkylamide bases would have unfavorable steric interactions with the *peri*-hydrogen at the 8-position as they approached the proton on the 1-position (inset of Scheme 6). Approach to the proton on the 3-position would lack this interaction and preferential deprotonation at the 3-position would be observed.[28] Initial attempts to lithiate **11a** with LDA (1.0−3.0 equiv) in THF at −78 °C were unsuccessful over a range of lithiation times (1 min−1.5 h), with quantitative recovery of amide **11a**. The use of lithium tetramethylpiperidide (LiTMP) was more successful (Table 1, entries 10−12). The addition of 3.0 equiv of LiTMP to a stirred solution of **11a** in THF at −78 °C with a 1.5 h lithiation time before addition of 3.0 equiv of the dichalcogenide electrophile **8-E** gave the 2,3-disubstituted regioisomers **16-E** in ≥50:1 regioselectivity. The 1,2-regioisomers **15-E** were present as ≤2% of the crude product mixture if present at all (Supporting Information for ^{1}H NMR spectra). As shown in Scheme 6, the dichalcogenide electrophile **8-E** had minimal impact on the reaction: sulfide **16-S** was isolated in 55% yield (91% based on recovered amide **11a**), 80% yield, selenide **16-Se** was isolated in 50% yield (94% based on recovered amide **11a**), and telluride **16-Te** was isolated in 53% yield (92% based on recovered amide **11a**). The regioselectivity of lithiation of **11a** with LiTMP was little affected by either shorter reaction times of **11a** with LiTMP (5 min to 1.5 h) or by the use of up to 6 equiv of LiTMP. Shorter reaction times or additional base gave reduced yields of **20-E**.

In solution, LiTMP is known to exist as cyclic oligomers and mixed aggregates as well as bis-solvated dimers, possibly decreasing its effectiveness in the directed ortho-lithiation of amide **11a**.[30−32] Additives such as TMEDA and LiBr are used to break up these aggregates, resulting in the formation of an "open-faced dimer" and monomer type species, respec-

Scheme 4. Metalation of Naphthamide 11a with *s*-BuLi/TMEDA Followed by Addition of Dichalcogenides 8-E and Cyclization with $POCl_3/Et_3N$

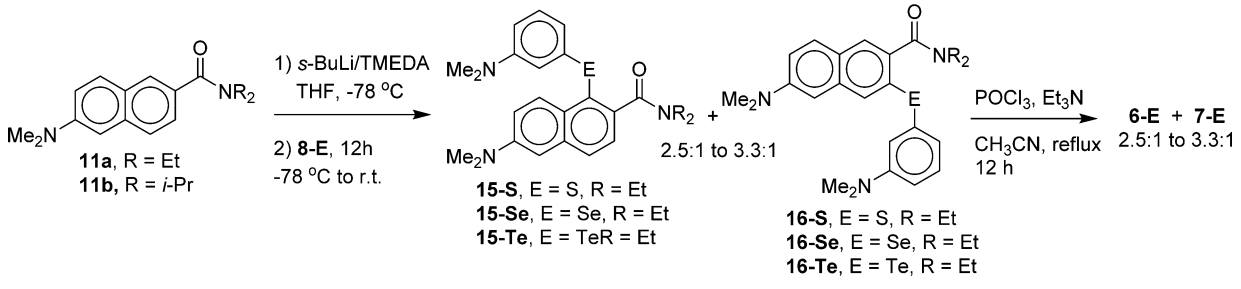


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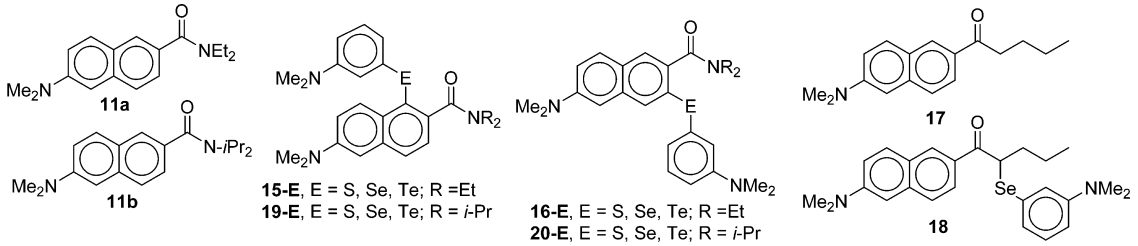
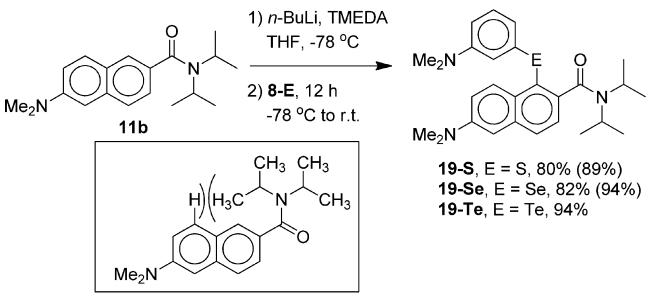
Table 1. Directed Metalations in 6-Dimethylamino-2-naphthamides 11 Followed by Quenching with Dichalcogenides 8-E to Give 1,2- and 2,3-Substituted Products



entry	amide	metalation conditions	electrophile	ratio 1,2 to 2,3-substitution
1	**11a**	*s*-BuLi/TMEDA, THF, −78 °C	**8-S**	2.5 (**15-S**):1 (**16-S**)
2	**11a**	*s*-BuLi/TMEDA, THF, −78 °C	**8-Se**	2.5 (**15-Se**):1 (**16-Se**)
3	**11a**	*s*-BuLi/TMEDA, THF, −78 °C	**8-Te**	3.3 (**15-Te**):1 (**16-Te**)
4	**11a**	*t*-BuLi, THF, −78 °C	**8-Se**	3 (**15-Se**):1 (**16-Se**)
5	**11a**	*n*-BuLi/TMEDA, THF, −78 °C	**8-Se**	–[a]
6	**11b**	*s*-BuLi/TMEDA, THF, −78 °C	**8-S**	2.5 (**19-S**):1 (**20-S**)
7	**11b**	*n*-BuLi/TMEDA, THF, −78 °C	**8-S**	50 (**19-S**):1 (**20-S**)
8	**11b**	*n*-BuLi/TMEDA, THF, −78 °C	**8-Se**	50 (**19-Se**):1 (**20-Se**)
9	**11b**	*n*-BuLi/TMEDA, THF, −78 °C	**8-Te**	25 (**19-Te**):1 (**20-Te**)
10	**11a**	LiTMP, THF, −78 °C	**8-S**	≤ 1 (**15-S**):50 (**16-S**)
11	**11a**	LiTMP, THF, −78 °C	**8-Se**	1 (**15-Se**):50 (**16-Se**)
12	**11a**	LiTMP, THF, −78 °C	**8-Te**	≤ 1 (**15-Te**):50 (**16-Te**)

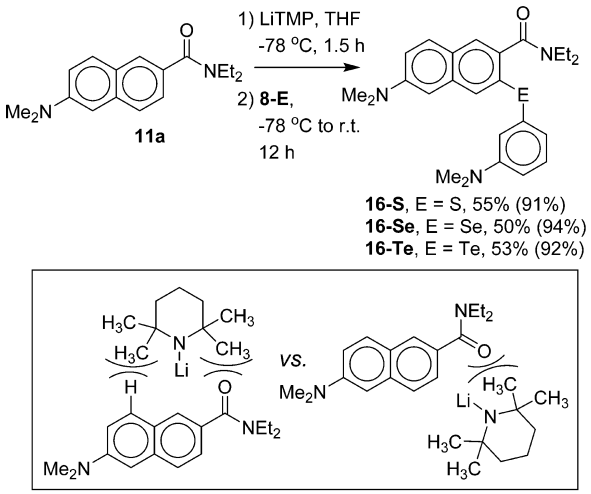
[a]Only products **17** and **18** were observed and were isolated in 40% and 30% yields, respectively.

Scheme 5. Regioselective Metalation of the 1-Position of *N,N*-Diisopropyl 2-naphthamide 11b[a]



[a]Yields in parentheses based on recovered starting material.

Scheme 6. Regioselective Metalation of the 3-Position of *N,N*-Diethyl 2-Naphthamide 11a[a]

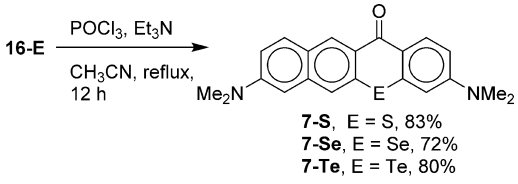


[a]Yields in parentheses are based on recovered starting material.

tively.[30,33,34] Neither LiTMP/TMEDA nor LiTMP-LiBr (3.0 equiv for each, 1.5 h lithiation time) had any effect on the overall yield of **16-E** relative to 3.0 equiv of LiTMP alone and a 1.5 h lithiation time.

While cyclization of the 1,2-disustituted diethylamides **15-E** in the **15-E**/**16-E** mixtures gave the corresponding extended xanthones **6-E**, attempts to cyclize the 1,2-disubstituted diisopropyl naphthamides **19-E** with $POCl_3$ and Et_3N[29] only returned unreacted **19-E**. The use of extended reaction times or the use of larger excesses of reagents did not give any of the desired extended xanthones **6-E**. In contrast, the cyclization of **16-E** with $POCl_3$ and Et_3N gave the extended xanthones **7-E** in 72% to 83% isolated yield as shown in Scheme 7. No other products were detected in the reaction mixtures.

Scheme 7. Cyclization of Chalcogenides 16-E to Xanthones 7-E



Strongly acidic conditions were used to cyclize 1,2-disubstituted naphthamides **19-E** successfully. While concentrated H_2SO_4 or Eaton's reagent (P_2O_5/methanesulfonic acid)[35] at 100 °C gave no product formation with recovery of unreacted **19-E**, treating naphthamides **19-E** with CF_3SO_3H at 140 °C for 72 h gave extended xanthones **6-E** in 51−62% isolated yield (Scheme 8). Dealkylated N-isopropyl naphthamides were also isolated from these reactions in <10% yield.

The dealkylated *N*-isopropyl naphthamides were examined as the potential precursors to **6-E**. When heated with CF_3SO_3H at 135 °C, **19-Se** gave *N*-isopropyl naphthamide **21-Se** as the

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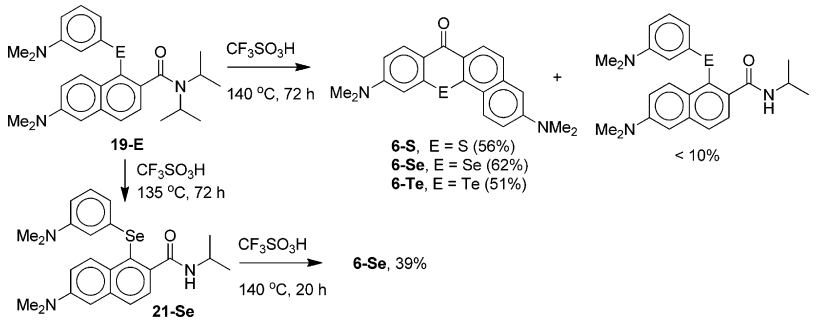
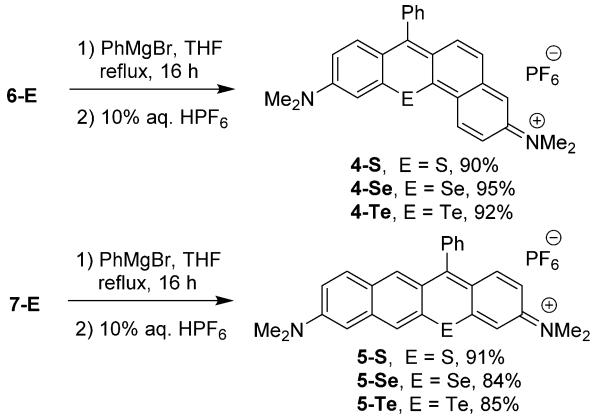
Scheme 8. Cyclization of 19-E with Trifluoromethanesulfonic Acid



predominant product in 61% yield (<10% **6-Se**). When isolated, **21-Se** was resubjected to the cyclization conditions (CF_3SO_3H, 140 °C) for 20 h, extended xanthone **6-Se** was isolated as the only product in 39% yield along with recovered **21-Se** (Scheme 8).

The addition of Grignard reagents to extended xanthones **6-E** and **7-E** leads directly to the extended rhodamine dyes. The addition of phenylmagnesium bromide to a stirred suspension of **6-E** or **7-E** in THF (16 h at reflux) followed by work up with 10% aqueous HPF_6 gave dyes **4-E** in 90% to 95% isolated yield or dyes **5-E** in 84% to 91% isolated yield (Scheme 9).

Scheme 9. Synthesis of Extended Rhodamine Dyes 4-E and 5-Se



Spectral and Photophysical Properties of Dyes 4-E and 5-E. The absorption spectra of the extended rhodamine dyes **4-E** and **5-E** in CH_2Cl_2 are shown in Figure 1. Values of λ_{max} in CH_2Cl_2, the molar extinction coefficient (ε) in CH_2Cl_2, the fluorescence emission maximum (λ_{FL}) in CH_2Cl_2, and the quantum yield for fluorescence (Φ_{FL}) in MeOH are compiled in Table 2. For comparison purposes, the same parameters for the tetramethylrosamines **1-E** are included in Table 2 as well. The dyes have a solubility of 1−2 mg mL^{-1} in MeOH and CH_2Cl_2.

The chromophores associated with dyes **4-E** and **5-E** have remarkably different wavelength distributions and bandwidths as shown in Figure 1. The absorption spectra of "bent" dyes **4-E** have values of λ_{max} for the major band that are 69−77 nm longer than the corresponding **1-E** analogue. Interestingly, bandwidths at half-height increase from 30 nm (670 cm^{-1}) for **4-Te** to 40 nm (920 cm^{-1}) for **4-Se** to 50 nm (1210 cm^{-1}) for **4-S** (Figure 1a). One possibility for the varying bandwidths is the formation of aggregates with **4-S** and **4-Se**. Formation of H-aggregates with dyes related in structure to dyes **1-E** has been documented when the dyes bind to TiO_2.[16−18] As a cursory probe of aggregation, bandwidths at half-height were measured over a range of concentrations (1×10^{-6} M to 2×10^{-5} M) and remained constant.

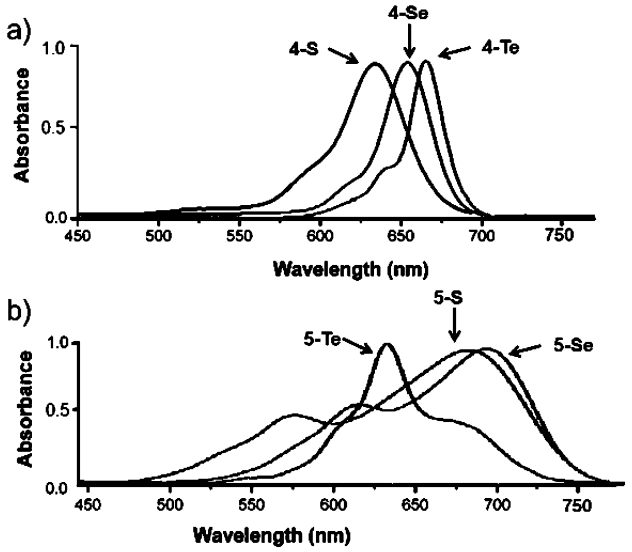


Figure 1. Absorption spectra in dichloromethane for (a) "bent" extended rhodamines **4-E** and (b) "linear" extended rhodamines **5-E**. Spectra are normalized to a common absorbance at λ_{max}.

Table 2. Values of Absorption Maxima (λ_{max}), Molar Extinction Coefficients (ε), and Fluorescence Emission Maxima (λ_{FL}) in CH_2Cl_2 and Quantum Yields for Fluorescence (Φ_{FL}) and for the Generation of Singlet Oxygen [$\Phi(^1O_2)$] in MeOH for 1-E, 4-E, and 5-E

cmpd	λ_{max}, nm	ε, M^{-1} cm^{-1}	λ_{FL}, nm	Φ_{FL}	$\Phi(^1O_2)$
1-S[a]	571	6.3×10^4	587	0.44	0.21
1-Se[a]	581	4.4×10^4	603	0.009	0.87
1-Te[b]	601	8.1×10^4		<0.005	0.43
4-S	641	6.5×10^4	715	0.47 ± 0.01	0.15
4-Se	658	6.9×10^4	717	0.009 ± 0.001	0.65
4-Te	670	6.6×10^4		<0.003	0.31
5-S	575	2.5×10^4	775	0.18 ± 0.01	<0.05
	689	4.9×10^4			
5-Se	610	2.7×10^4	781	0.009 ± 0.001	<0.05
	700	5.3×10^4			
5-Te	633	5.0×10^4		<0.003	<0.05
	675	2.7×10^4			

[a]Reference 11. [b]Reference 12.

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Organometallics XXXX, XXX, XXX−XXX

The spectral broadening in solution is even greater for dyes **5-E**. The bandwidths at half-height for **5-S** and **5-Se** are ≥100 nm for the long-wavelength bands (λ_{max} of 689 and 700 nm, respectively). As was observed with **4-Te**, the band structure is sharper in the spectrum of **5-Te** relative to its lighter chalcogen analogues **5-S** and **5-Se**. Values of λ_{max} are ≈120 nm longer for **5-S** and **5-Se** relative to **1-S** and **1-Se**, respectively. For **5-Te**, the shorter 633 nm band has stronger absorbance at λ_{max} than the longer-wavelength 675 nm band. Both of these bands have values of λ_{max} at longer wavelengths than λ_{max} for **1-Te** (601 nm). Again, as a cursory probe of aggregation, relative intensities of the various bands and bandwidths at half-height were measured over a range of concentrations (1×10^{-6} M to 2×10^{-5} M) and remained constant.

Values of Φ_{FL} were determined from steady-state fluorescence spectra for **4-S**, **4-Se**, **5-S**, **5-Se**, and **1-Se** (reference standard with Φ_{FL} = 0.009)[11] in MeOH with excitation at 532 nm (Table 2). Neither **4-Te** nor **5-Te** gave a detectable fluorescence and values of Φ_{FL} were arbitrarily assigned to be <0.003. Dye **4-S** has Φ_{FL} of 0.47, which is quite similar to the Φ_{FL} of 0.44 for **1-S**. Dyes **1-Se**, **4-Se**, and **5-Se** have identical vales of Φ_{FL} of 0.009. Dye **5-S** has Φ_{FL} of 0.18, which is lower than Φ_{FL} for **1-S** and **4-S**. The Stokes shifts for **1-S** and **1-Se** as defined by the wavelength difference between λ_{max} and λ_{FL} are 16 and 22 nm, respectively. For **4-S**, **4-Se**, and **5-S**, values of the Stokes shift are larger at 74 nm for **4-S**, 59 nm for **4-Se**, 86 nm for **5-S**, and 81 nm for **5-Se**.

Quantum yields for the generation of $^1O_2$ [$\Phi(^1O_2)$] by dyes **4-E** and **5-E** were measured by time-resolved spectroscopy at 1270 nm of $^1O_2$ luminescence in air-saturated methanol[36] using **1-Se** as a standard [$\Phi(^1O_2)$ = 0.87].[11] Values of $\Phi(^1O_2)$ for "bent" rhodamines **4-E** were comparable to their **1-E** analogue as shown in Table 2. Values of $\Phi(^1O_2)$ were determined to be 0.15 for **4-S**, 0.65 for **4-Se**, and 0.31 for **4-Te**. In contrast, the "linear" rhodamines **5-E** generated $^1O_2$ inefficiently with values of $\Phi(^1O_2)$ < 0.05 (Table 2).

DFT Calculations. The structures of **4-E** and **5-E** were optimized with DFT (B3LYP/6-311+G(d)/LanL2DZ). TD-DFT calculations were carried out on the optimized structures to analyze the electronic spectra of **4-E** and **5-E**. For all of the dyes **4-E**, the lowest energy excitation is due solely to the HOMO−LUMO transition (f = 0.67−0.75, Table 3). No other orbitals contribute to the low energy absorption. As shown in the frontier molecular orbitals (FMOs) of Figure 2, the HOMO is very cyanine-like with a node on the chalcogen atom for the **4-E** series. The energy of the HOMO is only slightly destabilized with heavy chalcogen substitution. The LUMO however is localized on the chalcogen atom and is stabilized with the heavier chalcogen atoms Se and Te. This results in the red-shifted electronic spectra as the size of the chalcogen atom increases. The calculated absorption spectra follow the trends observed in the experimental spectra with the exception of the high energy shoulder in the experimental spectra likely due to the formation of H-aggregates in solution (Supporting Information).

Table 3. Main Transitions, Oscillator Strengths (f), and Wavelengths (λ_{calcd}) Obtained by TD-DFT Calculations and the Corresponding Observed Wavelengths (λ_{obs}) for Dyes 4-E

ex1	main transition	f	λ_{calcd} (nm)	λ_{obs} (nm)
4-O	HOMO → LUMO	0.7248	522.7	
4-S	HOMO → LUMO	0.6981	550.2	641
4-Se	HOMO → LUMO	0.6701	560.8	658
4-Te	HOMO → LUMO	0.6765	570.0	670

For the dyes **5-E**, the lowest energy excitation is a combination of two excitations, both having contributions from the HOMO to LUMO and HOMO-1 to LUMO, (f_1 = 0.43−0.12, f_2 = 0.52−0.79, Table 4). As shown in Figure 3, both HOMO and LUMO energies of the **5-E** dyes are little affected by the heavy chalcogen atom substitution even though the chalcogen atom is contributing to both and the chalcogen atom contribution increases as the size of the chalcogen increases. The HOMO energy levels show a small increase in energy as the chalcogen atom increases in size from −8.08 eV for **5-O** to −8.00 eV for **5-Te** (Figure 3). The calculations also show that nitrogen contributions remain fairly constant in both HOMO and LUMO across the **5-E** series.

In contrast, the HOMO-1 increases in energy by 0.44 eV as the chalcogen atom increases in size from −8.82 eV for **5-O** to −8.38 eV for **5-Te** (Figure 3). The chalcogen contribution to the HOMO-1 also increases with increasing size of the chalcogen atom, but the most striking difference is in the contribution from the two nitrogen atoms. In **5-O**, the naphthalene-like nitrogen does not contribute to the HOMO-1. As the chalcogen atom contribution increases, the contribution of the naphthalene-like nitrogen also increases in the HOMO-1, which would increase the cyanine like character of this orbital.

The overlap of the chalcogen atom with the carbon π-framework can contribute to the spectral differences observed between the **4-E** and **5-E** series. The broadening is observed in the calculated spectra with two low energy transitions with contributions from the HOMO-1 and HOMO to LUMO (Supporting Information). For the tetramethylrosamines **1-E**, the relative contributions of anthracene-like resonance and cyanine-like resonance was a function of the chalcogen atom.[12] The anthracene-like contribution decreased as the chalcogen atom increased in size. As shown in Chart 2, the dyes **4-E** and **5-E** each have a cyanine-like resonance contributing to the chromophore as well as a benzanthracene-like resonance (benz[a]anthracene for **4-E** and benz[b]anthracene or tetracene for **5-E**). The benzanthracene contributions should decrease as the chalcogen atom increases in size while the cyanine contributions should increase. The calculations show this trend in the HOMO-1 orbitals for the **5-E** series with increasing cyanine character and decreasing tetracene character as the chalcogen atom increases in size. In the **4-E** series, the HOMO is essentially all cyanine in character with minimal contribution from the chalcogen atom.

CONCLUSIONS

The extended chalcogenorhodamine dyes **4-E** and **5-E** have been prepared with absorption maxima (λ_{max}) > 630 nm. Dyes **5-E** absorb light strongly out to 700 nm. The 630−700 nm optical window is important as it applies to photosensitizers for PDT (where penetration of light in tissue increases in the 600−800-nm window) and photosensitizers for the generation of solar electricity (harvesting of solar near-infrared light). Key to the synthesis of these chromophores is a highly regioselective synthesis of chalcogenoxanthones **6-E** and **7-E** as the precursors to the extended rhodamine dyes. The regioselective generation of 1-lithio-6-dimethylamino-2-naphthamide **9** or 3-lithio-6-dimethylamino-2-naphthamide **10** (Scheme 1) allowed

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Organometallics XXXX, XXX, XXX−XXX

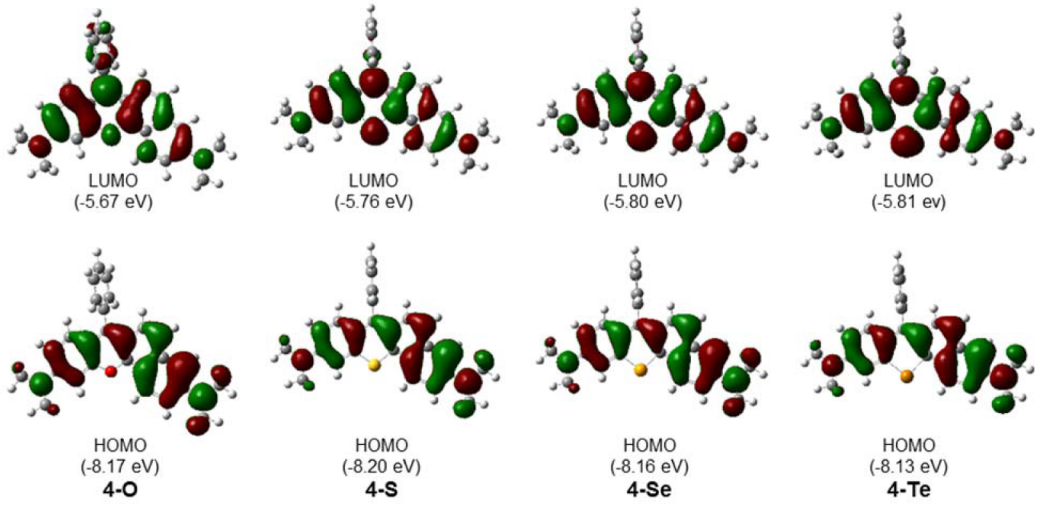

Figure 2. FMOs from DFT calculations for extended chalcogenorhodamine dyes **4-E** (E = O, S, Se, Te).

Table 4. Main Transitions, % Contributions, Oscillator Strengths (f), and Wavelengths (λ_{calcd}) Obtained by TD-DFT Calculations and Corresponding Observed Wavelengths (λ_{obs}) for Dyes 5-E

	main transitions					
cmpd	from	to	% contribution	f	λ_{calcd} (nm)	λ_{obs} (nm)
5-O	HOMO-1	LUMO	11.5	0.4275	589.0	
	HOMO	LUMO	87.2			
	HOMO-2	LUMO	3.1	0.5225	470.4	
	HOMO-1	LUMO	83.3			
	HOMO	LUMO	11.7			
5-S	HOMO-1	LUMO	15.2	0.3035	609.9	680
	HOMO	LUMO	83.4			
	HOMO-1	LUMO	82.3	0.5978	496.1	575
	HOMO	LUMO	14.7			
5-Se	HOMO-1	LUMO	18.5	0.2585	619.9	700
	HOMO	LUMO	80.4			
	HOMO-1	LUMO	79.7	0.6686	507.9	610
	HOMO	LUMO	17.9			
5-Te	HOMO-1	LUMO	21.3	0.173	644.7	675
	HOMO	LUMO	77.9			
	HOMO-1	LUMO	77.3	0.7904	523.4	633
	HOMO	LUMO	20.6			

the selective preparation of **6-E** and **7-E**, respectively. Increasing steric bulk in the naphthamide alkyl groups gave highly regioselective metalation of diisopropyl naphthamide **11b** at the 1-position with *n*-BuLi/TMEDA. Increasing steric bulk in a lithium dialkylamide gave highly regioselective metalation of diethyl naphthamide **11a** at the 3-position with LiTMP.

The solution absorption spectra of both the "bent" extended rhodamines **4-E** and the "linear" extended rhodamines **5-E** suggest that the chalcogen atom impacts the spectra through the effectiveness of overlap with the carbon π-framework. As the size of the chalcogen atom increases, benzanthracene-like resonance contributions decrease while cyanine-like contributions increase. The incorporation of aryl or heteroaryl groups bearing functionality for anchoring to TiO_2 or other semiconductors[16−18] in extended rhodamines **4-E** and **5-E** would generate extended rhodamine dyes that could be evaluated in DSSCs. Like their **1-E** analogues, the contributions of *H*- and/or *J*-aggregation on TiO_2 to the photoelectrical performance of these dyes could then be evaluated.

TD-DFT calculations show that the lowest energy absorption for **4-E** is from a HOMO to LUMO transition, and that the energy of the LUMO is more dependent on the chalcogen atom than the energy of the HOMO, which remains fairly constant across the chalcogen series. This trend is reversed in the **5-E** series where the LUMO remains constant across the chalcogen series and the energy of the HOMO is more chalcogen dependent. Dyes **5-E** have two low energy absorptions, with contributions from the HOMO-1 to LUMO transition as well as from the HOMO to LUMO transition. The energy of the HOMO-1 to LUMO transition is strongly dependent on the chalcogen atom. These two absorptions cause the broad peak in the experimental absorption spectra.

EXPERIMENTAL SECTION

Methyl 6-(Dimethylamino)-2-naphthoate (12).[37] Iodomethane (12.0 mL, 192 mmol) was added dropwise to a stirred solution of 6-amino-2-naphthoic acid (4.50 g, 24.0 mmol) and sodium carbonate (15.3 g, 144 mmol) in DMF (200 mL). The resulting mixture was heated at 110 °C for 16 h before being cooled to 60 °C and DABCO (4.05 g, 36.0 mmol) added. Heating was then resumed at 100 °C for 4 h. After cooling to ambient temperature, water (150 mL) was added and the product was extracted with diethyl ether (3 × 50 mL). The combined organic extracts were washed with water (3 × 100 mL), dried over anhydrous $MgSO_4$, and concentrated. The crude product was recrystallized from CH_2Cl_2/hexanes to give 5.46 g (99%) of **12** as a brown solid, mp 150−152 °C (literature[37] mp 148−149 °C): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (s, 1 H), 7.93 (dd, 1 H, J = 1.5, 9.0 Hz), 7.79 (d, 1 H, J = 9.0 Hz), 7.63 (d, 1 H, J = 9.0 Hz), 7.17 (dd, 1 H, J = 2.5, 9.5 Hz), 6.88 (d, 1 H, J = 2.5 Hz), 3.94 (s, 3 H), 3.10 (s, 6 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 167.6, 150.0, 137.5, 130.9, 130.3, 125.9, 125.7, 125.2, 123.0, 116.2, 105.3, 51.8, 40.4; IR (film on NaCl) 2949, 1714, 1624, 1508, 1436, 1384, 1290 cm^{-1}; HRMS (ESI, HRDFMagSec) m/z 230.1174 (calcd for $C_{14}H_{15}NO_2$ + H^+: 230.1176).

***N,N*-Diethyl 2-(6-Dimethylamino)naphthamide (11a).** *n*-Butyllithium (1.25 M, 8.37 mL, 10.5 mmol) was added dropwise to a stirred solution of diethylamine (1.17 mL, 11.3 mmol) in THF (30 mL) at −78 °C. The resulting mixture was stirred for 1 h and then transferred to a stirred solution of **12** (2.0 g, 8.72 mmol) in THF (50 mL) at ambient temperature. The resulting solution was heated at 45 °C for 30 min and then cooled to ambient temperature. A solution of

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Organometallics XXXX, XXX, XXX−XXX

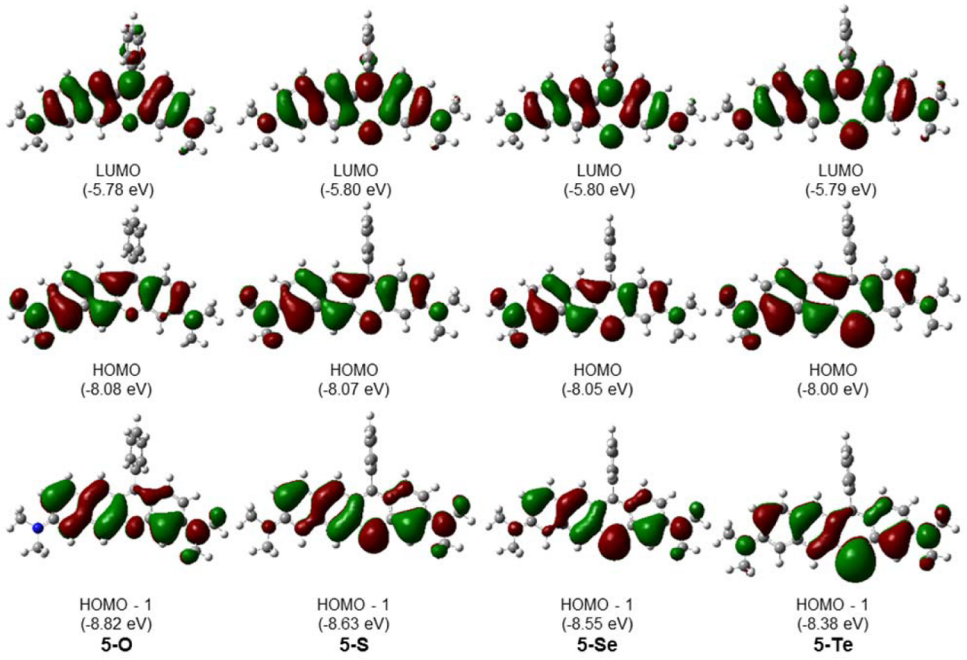
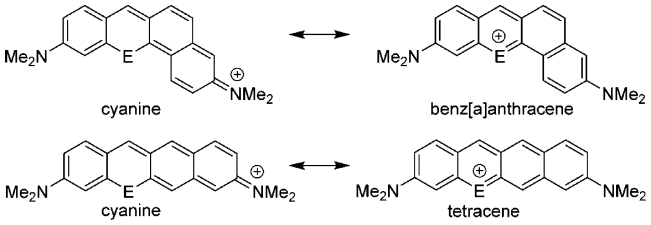


Figure 3. FMOs from DFT calculations for extended chalcogenorhodamine dyes **5-E** (E = O, S, Se, Te).

Chart 2. Cyanine and Benzanthracene Resonance Contributions to the π-Systems of Dyes 4-E and 5-E



saturated NH_4Cl (50 mL) was added, and products were extracted with CH_2Cl_2 (3 × 150 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated. The crude product was recrystallized from CH_2Cl_2/hexanes to give 2.29 g (97%) of **11a** as a yellow solid, mp 99−100 °C. Purity was assessed by NMR spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (s, 1 H), 7.71 (d, 1 H, J = 9.0 Hz), 7.65 (d, 1 H, J = 8.5 Hz), 7.37 (dd, 1 H, J = 2.0, 8.5 Hz), 7.18 (dd, 1 H, J = 2.5, 9.0 Hz), 6.90 (d, 1 H, J = 2.5 Hz), 3.69−3.26 (m, 4 H), 3.07 (s, 6 H), 1.40−1.06 (m, 6 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 171.5, 148.8, 134.9, 130.1, 128.8, 125.8, 125.5, 125.4, 124.2, 116.4, 105.4, 43.3, 40.2, 39.1, 13.4; IR (film on NaCl) 2970, 2890, 2750, 1627, 1506, 1420, 1382 cm^{-1}; HRMS (ESI, HRDFMagSec) m/z 271.1805 (calcd for $C_{17}H_{22}N_2O$ + H^+: 271.1805).

***N,N*-Diisopropyl 2-(6-Dimethylamino)naphthamide (11b).** *n*-Butyllithium (1.25 M, 4.89 mL, 6.11 mmol) was added dropwise to a stirred solution of diisopropylamine (978 μL, 6.98 mmol) in THF (15 mL) at −78 °C. The resulting mixture was stirred for 1 h then transferred to a stirred solution of **12** (1.0 g, 4.36 mmol) in THF (20 mL) at ambient temperature. The resulting solution was heated at 45 °C for 30 min and then cooled to ambient temperature. A solution of saturated NH_4Cl (50 mL) was added, and products were extracted with CH_2Cl_2 (3 × 150 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated. The crude product was recrystallized from CH_2Cl_2/hexanes to give 1.10 g (85%) of **11b** as an orange solid, mp 148−150 °C. Purity was assessed by NMR spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, 1 H, J = 9.5 Hz), 7.65 (s, 1 H), 7.64 (d, 1 H, J = 8.0 Hz), 7.31 (dd, 1 H, J = 2.0, 9.0 Hz), 7.18 (dd, 1 H, J = 3.0, 9.5), 6.90 (d, 1 H, J = 3.0 Hz), 3.77 (br s, 2 H), 3.06 (s, 6 H), 1.37 (br s, 12 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 171.5, 149.0, 134.8, 132.3, 129.0, 126.1, 125.8, 124.8, 123.9, 116.7, 105.9, 47.5 (br), 40.6, 20.8. IR (film on NaCl) 2968, 2927, 1627, 1505, 1436, 1378, 1335 cm^{-1}; HRMS (EI, HRDFMagSec) m/z 298.2047 (calcd for $C_{19}H_{26}N_2O$: 298.2040).

General Procedure for Metalation of Naphthamide 11a with *s*-BuLi and Quenching with Dichalcogenides 8-E. *s*-Butyllithium (0.87 M, 4.46 mL, 3.88 mmol) was added dropwise to a stirred solution of naphthamide **11a** (1.0 g, 3.70 mmol) and TMEDA (606 μL, 4.07 mmol) in THF (75 mL) at −78 °C. A solution of disulfide **8-S**[22] (2.25 g, 7.39 mmol), **8-Se**[22] (2.94 g, 7.39 mmol), or **8-Te**[29] (3.66 g, 7.39 mmol) in THF (30 mL) at −78 °C was immediately added, and the resulting mixture was stirred at −78 °C for 3 h and then warmed to ambient temperature with stirring overnight (12 h). A solution of saturated NH_4Cl (50 mL) was added, and products were extracted with CH_2Cl_2 (3 × 150 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated. The crude products were purified via chromatography on SiO_2 eluted with 0.5:9.5 Et_2O/CH_2Cl_2 (R_f = 0.5) to give 1.43 g (91%) of a mixture of **15-S** and **16-S**, 1.61 g (93%) of a mixture of **15-Se** and **16-Se**, and 1.74 g (91%) of a mixture of **15-Te** and **16-Te**. These mixtures were used without further purification or separation. ^{1}H NMR spectra of mixtures are in the Supporting Information. For **15-S**/**16-S**: HRMS (EI, HRDFMagSec) m/z 421.2182 (calcd for $C_{25}H_{31}N_3OS$: 421.2182). For **15-Se**/**16-Se**: HRMS (ESI, HRDFMagSec) m/z 470.1690 (calcd for $C_{25}H_{31}N_3O^{80}Se$ + H^+: 470.1705. For **15-Te**/**16-Te**: HRMS (ESI, HRDFMagSec) m/z 520.1688 (calcd for $C_{25}H_{31}N_3O^{130}Te$ + H^+: 520.1602).

***N,N*-Diethyl Naphthamide 16-S.** *n*-Butyllithium (2.00 M, 2.77 mL, 5.55 mmol) was added dropwise to a stirred solution of 2,2,6,6-tetramethylpiperidine (1.03 mL, 6.10 mmol) in THF (20 mL) at 0 °C. The resulting mixture was stirred for 15 min then transferred to a stirred solution of naphthamide **11a** (500 mg, 1.85 mmol) in THF (20 mL) at −78 °C. The resulting solution was stirred at −78 °C for 1.5 h and a solution of disulfide **8-S**[22] (1.69 g, 5.55 mmol) in THF (30 mL) at −78 °C was added. The resulting mixture was stirred at −78 °C for 3.5 h and then 12 h at ambient temperature. A solution of saturated NH_4Cl (50 mL) was added and products extracted with CH_2Cl_2 (3 × 150 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified via gradient column chromatography on SiO_2 (1:4 EtOAc/hexanes to 1:1 EtOAc/hexanes) to give 429 mg (55%) of **16-S** as a yellow oil (91% based on recovered **11a**). Purity was assessed by NMR spectroscopy: ^{1}H NMR

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Organometallics XXXX, XXX, XXX−XXX

(300 MHz, CD_2Cl_2) δ 7.65 (d, 1 H, J = 8.7 Hz), 7.51 (s, 1 H), 7.45 (s, 1 H), 7.18 (t, 1 H, J = 8.4 Hz), 7.14 (dd, 1 H, J = 3.0, 8.7 Hz), 6.85 (s, 1 H), 6.74 (d, 1 H, J = 7 Hz), 6.70 (s, 1 H), 6.67 (d, 1 H, J = 8.5 Hz), 3.71−3.50 (m, 2 H), 3.31−3.18 (m, 2 H), 3.02 (s, 6 H), 2.94 (s, 6 H), 1.32 (t, 3 H, J = 6.9 Hz), 1.10 (t, 3 H, J = 6.9 Hz); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 169.4, 151.5, 149.6, 135.5, 135.2, 132.7, 131.9, 130.0, 128.8, 128.3, 125.5, 124.9, 120.3, 116.8, 116.3, 112.0, 105.1, 43.3, 40.6, 40.5, 39.2, 14.2, 12.9; IR (film on NaCl) 2972, 2930, 2820, 1623, 1589, 1503, 1444, 1382 cm^{-1}; HRMS (EI, HRDFMagSec) m/z 421.2182 (calcd for $C_{25}H_{31}N_3OS$: 421.2182).

_N,N_-Diethyl Naphthamide 16-Se. _n_-Butyllithium (2.22 M, 2.50 mL, 5.55 mmol), 2,2,6,6-tetramethylpiperidine (1.03 mL, 6.10 mmol), naphthamide **11a** (500 mg, 1.85 mmol), and diselenide **8-Se**[22] (2.21 g, 5.55 mmol) in THF were treated as described for the preparation of **16-S**. The crude product was purified via gradient column chromatography (SiO_2, 1:4 EtOAc/hexanes to 1:1 EtOAc/hexanes) to give 436 mg (50%) of **16-Se** as a yellow oil (94% based on recovered **11a**). Purity was assessed by NMR spectroscopy: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.72−7.64 (m, 2 H), 7.57 (s, 1 H), 7.20 (t, 1 H, J = 8.0 Hz), 7.14 (d, 1 H, J = 3.5 Hz), 7.05 (s, 1 H), 6.94 (d, 1 H, J = 7.5 Hz), 6.76−6.68 (m, 2 H), 3.71−3.58 (m, 2 H), 3.36−3.24 (m, 2 H), 3.00 (s, 6 H), 2.94 (s, 6 H), 1.44−1.30 (m, 3 H), 1.20−1.08 (m, 3 H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 170.1, 151.6, 149.6, 135.8, 133.3, 131.0, 130.1, 130.0, 128.9, 128.2, 125.2, 124.9, 122.4, 118.4, 116.8, 112.2, 105.0, 43.5, 40.7, 40.5, 39.3, 14.4, 12.9; IR (film on NaCl) 2990, 2930, 2800, 1622, 1588, 1498, 1444, 1381 cm^{-1}; HRMS (ESI, HRDFMagSec) m/z 470.1690 (calcd for $C_{25}H_{31}N_3O^{80}Se$ + H^+: 470.1705).

_N,N_-Diethyl Naphthamide 16-Te. _n_-Butyllithium (2.22 M, 1.39 mL, 2.77 mmol), 2,2,6,6-tetramethylpiperidine (515 μL, 3.05 mmol), **11a** (250 mg, 0.925 mmol), and ditelluride **8-Te**[29] (1.37 g, 2.77 mmol) in THF were treated as described for the preparation of **16-S**. The crude product was purified via gradient column chromatography (SiO_2, 1:4 EtOAc/hexanes to 1:1 EtOAc/hexanes) to give 254 mg (53%) of **16-Te** as a yellow oil (92% based on recovered **11a**). Purity was assessed by NMR spectroscopy: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.82 (s, 1 H), 7.68 (d, 1 H, J = 9.3 Hz), 7.62 (s, 1 H), 7.37 (d, 1 H, J = 1.8 Hz), 7.28 (d, 1 H, J = 6.9 Hz), 7.16 (t, 1 H, J = 8.4 Hz), 7.13 (dd, 1 H, J = 2.4, 8.7 Hz), 6.76 (dd, 1 H, J = 2.4, 8.4 Hz), 6.64 (d, 1 H, J = 2.4), 3.66−3.40 (m, 4 H), 3.00 (s, 6 H), 2.95 (s, 6 H), 1.41−1.18 (m, 6 H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 171.9, 151.5, 149.5, 136.2, 134.0, 133.8, 130.1, 129.1, 128.0, 125.1, 124.6, 124.0, 116.7, 116.6, 115.5, 112.6, 104.7, 40.6, 40.5, 40.4, 13.8; IR (film on NaCl) 2970, 2940, 2900, 1619, 1582, 1502, 1443, 1420, 1382 cm^{-1}; HRMS (ESI, HRDFMagSec) m/z 520.1602 (calcd for $C_{25}H_{31}ON_3{}^{130}Te$ + H^+: 520.1602).

_N,N_-Diisopropyl Naphthamide 19-S. _n_-Butyllithium (2.05 M, 450 μL, 0.838 mmol) was added dropwise to a stirred solution of naphthamide **11b** (250 mg, 0.921 mmol) and TMEDA (137 μL, 0.921 mmol) in THF (20 mL) at −78 °C. The resulting mixture was stirred for 30 min before adding a solution of disulfide **8-S**[22] (281 mg, 0.921 mmol) in THF (20 mL) at −78 °C. The resulting mixture was stirred at −78 °C for 3 h and then 15 h at ambient temperature. A solution of saturated NH_4Cl (50 mL) was added, and products were extracted with CH_2Cl_2 (3 × 150 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified via column chromatography (SiO_2, 1:9 Et_2O/CH_2Cl_2, R_f = 0.4) followed by recrystallization from CH_3CN to give 302 mg (80%) of **19-S** (89% based on recovered **11b**) as a yellow solid, mp 174−175 °C. Purity was assessed by NMR spectroscopy: ^{1}H NMR (500 MHz, CD_3Cl) δ 8.24 (d, 1 H, J = 9.0 Hz), 7.72 (d, 1 H, J = 8.5 Hz), 7.24 (d, 1 H, J = 8.0 Hz), 7.14 (dd, 1 H, J = 9.5, 3.0 Hz), 6.94 (t, 1 H, J = 8.5 Hz), 6.89 (d, 1 H, J = 2.5 Hz), 6.62 (s, 1 H), 6.41 (dd, 1 H, J = 8.0, 2.5 Hz), 6.34 (d, 1 H, J = 8.5 Hz), 3.70 (septet, 1 H, J = 6.5 Hz), 3.48 (septet, 1 H, J = 7.0 Hz), 3.03 (s, 6 H), 2.81 (s, 6 H), 1.62−1.57 (m, 6 H), 1.05 (d, 3 H, J = 6.5 Hz), 0.92 (d, 3 H, J = 7.0 Hz); ^{13}C NMR (75.5 MHz, CD_3Cl) δ 169.5, 150.6, 148.6, 139.5, 138.6, 135.1, 129.1, 128.8, 127.6, 127.4, 124.5, 123.4, 117.3, 115.4, 111.1, 109.5, 106.2, 50.8, 45.6, 40.3, 40.2, 20.7, 20.6, 20.2; IR (film on NaCl) 2967, 2814, 1619, 1588, 1499, 1445, 1369, 1335 cm^{-1}; HRMS (ESI, HRDFMagSec) m/z 450.2556 (calcd for $C_{27}H_{35}N_3OS$ + H^+: 450.2574).

_N,N_-Diisopropyl Naphthamide 19-Se. _n_-Butyllithium (1.95 M, 567 μL, 1.10 mmol), naphthamide **11b** (300 mg, 1.00 mmol), TMEDA (165 μL, 1.10 mmol), and diselenide **8-Se**[22] (440 mg, 1.10 mmol) in THF were treated as described for the preparation of **19-S**. The crude product was purified via column chromatography on SiO_2 (1:9 Et_2O/CH_2Cl_2, R_f = 0.4) followed by recrystallization out of CH_3CN to give 387 mg (82%) of **19-Se** (94% based on recovered **11b**) as a yellow solid, mp 178−179 °C. Purity was assessed by NMR spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, 1 H, J = 9.0 Hz), 7.71 (d, 1 H, J = 8.5 Hz), 7.23 (d, 1 H, J = 8.5 Hz), 7.12 (dd, 1 H, J = 2.5, 9.0 Hz), 6.91 (t, 1 H, J = 8.0 Hz), 6.88 (d, 1 H, J = 2.5 Hz), 6.70 (s, 1 H), 6.46−6.41 (m, 2 H), 3.74 (septet, 1 H, J = 6.5 Hz), 3.48 (septet, 1 H, J = 7.0 Hz), 3.03 (s, 6 H), 2.80 (s, 6 H), 1.61 (d, 3 H, J = 6.5 Hz), 1.59 (d, 3 H, J = 7.0 Hz), 1.05 (d, 3 H, J = 6.5 Hz), 0.911 (d, 3 H, J = 7.0 Hz); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 170.3, 151.4, 149.2, 140.7, 135.5, 134.2, 130.1, 129.6, 129.2, 127.9, 123.6, 123.4, 118.0, 117.6, 113.9, 110.5, 106.6, 51.3, 46.0, 40.6, 40.4, 20.9, 20.8, 20.7, 20.5; IR (film on NaCl) 2967, 2938, 1618, 1588, 1497, 1445, 1368, 1331 cm^{-1}; HRMS (ESI, HRDFMagSec) m/z 498.2020 (calcd for $C_{27}H_{35}N_3O^{80}Se$ + H^+: 498.2018).

_N,N_-Diisopropyl Naphthamide 19-Te. _n_-Butyllithium (1.95 M, 476 μL), naphthamide **11b** (250 mg, 0.838 mmol), TMEDA (250 mg, 0.838 mmol), and ditelluride **8-Te**[29] (457 mg, 0.921 mmol) in THF were treated as described for the preparation of **19-S**. The crude product was purified via column chromatography on SiO_2 (1:9 Et_2O/CH_2Cl_2, R_f = 0.4) followed by recrystallization from CH_3CN to give 429 mg (94%) of **19-Te** as a yellow solid, mp 184−185 °C. Purity was assessed by NMR spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, 1 H, J = 9.5 Hz), 7.70 (d, 1 H, J = 8.0 Hz), 7.21 (d, 1 H, J = 8.5 Hz), 7.08 (dd, 1 H, J = 3.0, 9.5 Hz), 6.90−6.83 (m, 2 H), 6.79 (s, 1 H), 6.59 (d, 1 H, J = 8.0 Hz), 6.46 (dd, 1 H, J = 2.5, 8.5 Hz), 3.83 (septet, 1 H, J = 7.0 Hz), 3.49 (septet, 1 H, J = 6.5 Hz), 3.03 (s, 6 H), 2.77 (s, 6 H), 1.64 (d, 3 H, J = 7.0 Hz), 1.59 (d, 3 H, J = 7.0 Hz), 1.09 (d, 3 H, J = 6.5 Hz), 0.976 (d, 3 H, J = 6.5 Hz); ^{13}C NMR (125.5 MHz, $CDCl_3$) δ 171.8, 150.7, 148.5, 143.3, 134.6, 134.0, 129.4, 128.9, 128.8, 122.7, 122.5, 118.3, 117.3, 117.2, 113.2, 110.7, 106.1, 51.0, 45.6, 40.3, 40.0, 20.6, 20.5, 20.2, 20.1; IR (film on NaCl) 2968, 2929, 2802, 1620, 1584, 1496, 1444, 1367, 1338 cm^{-1}; HRMS (ESI, HRDFMagSec) m/z 548.1912 (calcd for $C_{27}H_{35}N_3O^{130}Te$ + H^+: 548.1915).

Preparation of Ketones 17 and 18. _n_-Butyllithium (2.22 M, 458 μL, 1.02 mmol) was added dropwise to a stirred solution of naphthamide **11a** (250 mg, 0.925 mmol) and TMEDA (152 μL, 1.02 mmol) in THF (20 mL) at −78 °C. The resulting mixture was stirred for 1 min before adding a solution of diselenide 8-Se[22] (405 mg, 1.02 mmol) in THF (20 mL) at −78 °C with continued stirring at −78 °C for 3 h and then 15 h at ambient temperature. A solution of saturated NH_4Cl (50 mL) was added, and products were extracted with CH_2Cl_2 (3 × 150 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified via column chromatography on SiO_2 (1:4 EtOAc/hexanes, R_f = 0.5 and 0.9) to give 94 mg (40%) of **17** as a brown solid, mp 80−81 °C, and 126 mg (30%) of **18** as a dark orange oil. Purity was assessed by NMR spectroscopy.

For **17**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, 1 H, J = 2.0 Hz), 7.93 (dd, 1 H, J = 2.0, 9.0 Hz), 7.80 (d, 1 H, J = 9.5 Hz), 7.64 (d, 1 H, J = 8.5 Hz), 7.17 (dd, 1 H, J = 2.5, 9.0 Hz), 6.88 (d, 1 H, J = 2.5 Hz), 3.11 (s, 6 H), 3.04 (t, 2 H, J = 7.5 Hz), 1.77 (quintet, 2 H, J = 7.0 Hz), 1.45 (sextet, 2 H, J = 7.5 Hz), 0.975 (t, 3 H, J = 7.0 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 200.0, 150.0, 137.5, 130.5, 130.4, 129.7, 126.0, 124.9, 124.5, 116.1, 105.1, 40.2, 37.9, 26.8, 22.5, 13.9; IR (film on NaCl) 2951, 2918, 2850, 1654, 1616, 1506, 1383, 1340 cm^{-1}; HRMS (ESI, HRDFMagSec) m/z 256.1689 (calcd for $C_{17}H_{21}NO$ + H^+: 256.1696).

For **18**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, 1 H, J = 1.5 Hz), 7.94 (dd, 1 H, J = 1.5, 9.0 Hz), 7.64−7.58 (m, 2 H), 7.11−7.15 (m, 2 H), 6.93 (d, 1 H, J = 7.5 Hz), 6.85 (d, 1 H, J = 2.5 Hz), 6.79 (s, 1 H), 6.65 (dd, 1 H, J = 2.0, 8.0 Hz), 4.69 (dd, 1 H, J = 1.0, 7.0 Hz), 3.09 (s,

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Organometallics XXXX, XXX, XXX−XXX

6 H), 2.80 (s, 6 H), 2.28−2.19 (m, 1 H), 2.07−1.98 (m, 1 H), 1.66−1.57 (m, 1 H), 1.56−1.48 (m, 1 H), 0.989 (t, 3 H, J = 7.0 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 196.3, 150.5, 150.1, 137.4, 130.7, 130.1, 129.7, 129.3, 129.1, 125.9, 125.0, 124.9, 123.5, 119.9, 115.9, 112.5, 105.1, 46.2, 40.3, 40.1, 33.8, 21.5, 13.9; IR (film on NaCl) 2956, 2928, 1657, 1619, 1588, 1494, 1444, 1384, 1348 cm^{-1}; HRMS (ESI, HRDFMagSec) m/z 455.1598 (calcd for $C_{25}H_{30}N_2O^{80}Se$ + H^+: 455.1596).

Diaryl Selenide 21-Se. Selenide **19-Se** (200 mg, 0.403 mmol) was dissolved in CF_3SO_3H (5 mL) and the resulting mixture heated at 135 °C for 48 h. The reaction mixture was cooled to 0 °C and carefully diluted with cold distilled water (25 mL). Cold 1 M NaOH was added until the reaction mixture was basic (pH ≈ 10). The resulting mixture was stirred for 6 h and products were extracted with CH_2Cl_2 (3 × 250 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified via column chromatography on SiO_2 (1:9 Et_2O/CH_2Cl_2, R_f = 0.3) followed by recrystallization from CH_2Cl_2/hexanes to give 112 mg (61%) of **21-Se** as a yellow solid, mp 124−125 °C. Purity was assessed by NMR spectroscopy: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.46 (d, 1 H, J = 9.3 Hz), 7.73 (d, 1 H, J = 8.1 Hz), 7.52 (d, 1 H, J = 8.4 Hz), 7.16 (dd, 1 H, J = 2.7, 9.3 Hz), 6.94 (t, 1 H, J = 8.1 Hz), 6.87 (d, 1 H, J = 2.1 Hz), 6.59 (s, 1 H), 6.45 (dd, 1 H, J = 2.4, 8.4 Hz), 6.31 (d, 1 H, J = 7.5 Hz), 5.75 (d, 1 H, J = 7.8 Hz), 4.28−4.12 (m, 1 H), 3.06 (s, 6 H), 2.80 (s, 6 H), 1.08 (d, 6 H, J = 6.3 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 169.4, 151.1, 149.0, 138.7, 135.9, 134.8, 130.6, 129.8, 128.7, 128.1, 125.6, 123.4, 117.4, 116.4, 112.3, 110.2, 106.0, 42.0, 40.4, 40.3, 22.3; IR (film on NaCl) 3259, 2968, 1617, 1587, 1497, 1443, 1367, 1254 cm^{-1}; HRMS (ESI, HRDFMagSec) m/z 456.1561 (calcd for $C_{24}H_{29}N_3O^{80}Se$ + H^+: 456.1559).

Extended Thioxanthone 6-S. Diaryl sulfide **19-S** (162 mg, 0.360 mmol) was dissolved in CF_3SO_3H (3 mL) and the resulting mixture heated at 140 °C for 72 h. The reaction mixture was cooled to 0 °C and carefully diluted with cold distilled water (25 mL). Cold 1 M NaOH was added until the reaction mixture was basic (pH ≈ 10). The resulting mixture was stirred for 6 h, and products were extracted with CH_2Cl_2 (3 × 250 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified via column chromatography on SiO_2 (1:9 Et_2O/CH_2Cl_2, R_f = 0.7) followed by recrystallization from CH_2Cl_2/hexanes to give 79 mg (56%) of **6-S** as a yellow solid, mp >260 °C. Purity was assessed by NMR spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46−8.50 (m, 2 H), 8.20 (d, 1 H, J = 9.5 Hz), 7.59 (d, 1 H, J = 9.0 Hz), 7.18 (dd, 1 H, J = 2.5, 9.0 Hz), 6.90 (d, 1 H, J = 2.5 Hz), 6.85 (dd, 1 H, J = 2.5, 9.5 Hz), 6.73 (d, 1 H, J = 2.0 Hz), 3.16−3.09 (m, 12 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 178.8, 151.9, 150.2, 138.2, 136.6, 136.2, 130.8, 125.3, 124.8, 124.5, 124.4, 120.9, 118.9, 115.3, 112.0, 106.6, 105.4, 40.3, 40.0; IR (film on NaCl) 2925, 1614, 1587, 1507, 1406, 1370, 1335 cm^{-1}; HRMS (EI, HRDFMagSec) m/z 348.1291 (calcd for $C_{21}H_{20}N_2OS^+$: 348.1291).

Extended Selenoxanthone 6-Se. Diaryl selenide **19-Se** (150 mg, 0.302 mmol) and CF_3SO_3H (3 mL) were treated as described for the preparation of **6-S**. The crude product was purified via column chromatography on SiO_2 (1:9 Et_2O/CH_2Cl_2, R_f = 0.7) followed by recrystallization from CH_2Cl_2/hexanes to give 74 mg (62%) of **6-Se** as a yellow solid, mp >260 °C. Purity was assessed by NMR spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56−8.51 (m, 2 H), 7.97 (d, 1 H, J = 9.5 Hz), 7.59 (d, 1 H, J = 9.0 Hz), 7.19 (dd, 1 H, J = 2.0, 9.0 Hz), 6.89 (d, 1 H, J = 2.5 Hz), 6.85−6.80 (m, 2 H), 3.12 (s, 6 H), 3.11 (s, 6 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 180.9, 151.8, 150.1, 136.4, 136.2, 135.9, 132.2, 126.7, 126.2, 124.8, 122.7, 120.1, 115.5, 112.0, 107.8, 106.4, 40.3, 40.0; IR (film on NaCl) 2932, 1606, 1582, 1507, 1407, 1372, 1329 cm^{-1}; HRMS (EI, HRDFMagSec) m/z 396.0742 (calcd for $C_{21}H_{20}N_2O^{80}Se^+$: 396.0742).

Extended Telluroxanthone 6-Te. Diaryl Telluride **19-Te** (156 mg, 0.286 mmol) and CF_3SO_3H (3 mL) were treated as described for the preparation of **6-S**. The crude product was purified via chromatography on SiO_2 (1:9 Et_2O/CH_2Cl_2, R_f = 0.7) followed by recrystallization from CH_2Cl_2/hexanes to give 65 mg (51%) of **6-Te** as a yellow solid, mp >260 °C. Purity was assessed by NMR spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62−8.56 (m, 2 H), 7.61−7.54 (m, 2 H), 7.17 (dd, 1 H, J = 2.5, 9.0 Hz), 6.90 (d, 1 H, J = 2.5 Hz), 6.87 (d, 1 H, J = 2.5 Hz), 6.79 (dd, 1 H, J = 2.5, 9.0 Hz), 3.11 (s, 6 H), 3.09 (s, 6 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 185.1, 151.6, 150.1, 136.2, 133.7, 130.2, 129.3, 128.5, 126.1, 125.5, 125.2, 123.0, 121.2, 115.6, 113.5, 112.4, 106.4, 40.3, 39.9; IR (film on NaCl) 2922, 1602, 1574, 1506, 1438, 1402, 1365, 1314 cm^{-1}; HRMS (ESI, HRDFMagSec) m/z 447.0713 (calcd for $C_{21}H_{20}N_2O^{130}Te$ + H^+: 447.0711).

Extended Thioxanthone 7-S. Phosphorus oxychloride (1.14 mL, 12.2 mmol) was added dropwise to a solution of Et_3N (1.79 mL, 12.2 mmol) and **16-S** (429 mg, 1.02 mmol) in CH_3CN (25 mL). The resulting mixture was heated at reflux for 12 h and then cooled to 0 °C. A solution of 1 M NaOH (10 mL) was added slowly, and the resulting mixture was poured into a stirred solution of cold 1 M NaOH (200 mL), stirred for 6 h, and products were extracted with CH_2Cl_2 (3 × 250 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated. The resulting solid was recrystallized from CH_2Cl_2/hexanes to give 294 mg (83%) of **7-S** as an orange solid, mp >250 °C. Purity was assessed by NMR spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.97 (s, 1 H), 8.46 (d, 1 H, J = 9.0 Hz), 7.89 (d, 1 H, J = 9.5 Hz), 7.68 (s, 1 H), 7.16 (dd, 1 H, J = 2.5, 9.0 Hz), 6.60−6.80 (m, 2 H), 6.60 (m, 1 H); 3.12 (s, 6 H), 3.11 (s, 6 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 179.4, 152.3, 150.3, 139.7, 136.6, 132.6, 131.5, 131.1, 130.6, 124.8, 123.9, 120.3, 118.6, 116.3, 110.9, 105.1, 102.9, 40.4, 40.1; IR (film on NaCl) 1613, 1591, 1500, 1441, 1389, 1371, 1336, 1286 cm^{-1}; HRMS (ESI, HRDFMagSec) m/z 349.1369 (calcd for $C_{21}H_{20}N_2OS$ + H^+: 349.1370).

Extended Selenoxanthone 7-Se. Phosphorus oxychloride (931 μL, 9.99 mmol), Et_3N (1.39 mL, 9.99 mmol) and **16-Se** (390 mg, 0.832 mmol) in CH_3CN (25 mL) were treated as described for the preparation of **7-S**. The resulting solid was recrystallized from CH_2Cl_2/hexanes to give 247 mg (72%) of **7-Se** as an orange solid, mp >250 °C. Purity was assessed by NMR spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.02 (s, 1 H), 8.50 (d, 1 H, J = 9.0 Hz), 7.87 (d, 1 H, J = 9.0 Hz), 7.75 (s, 1 H), 7.15 (dd, 1 H, J = 2.5, 9.0 Hz), 6.78−6.72 (m, 2 H), 6.69 (s, 1 H, J = 3.0 Hz), 3.11 (s, 6 H), 3.09 (s, 6 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 181.3, 152.2, 150.3, 136.8, 136.7, 132.8, 132.0, 131.2, 129.5, 125.2, 125.0, 123.0, 120.2, 116.2, 111.1, 107.9, 102.8, 40.4, 40.0; IR (film on NaCl) 2949, 1610, 1588, 1498, 1438, 1389, 1328 cm^{-1}; HRMS (EI, HRDFMagSec) m/z 396.0733 (calcd for $C_{21}H_{20}N_2O^{80}Se^+$: 396.0735).

Extended Telluroxanthone 7-Te. Phosphorus oxychloride (748 μL, 8.03 mmol), Et_3N (1.12 mL, 8.03 mmol) and **16-Te** (346 mg, 0.669 mmol) in CH_3CN (25 mL) were treated as described for the preparation of **7-S**. The resulting solid was recrystallized from CH_2Cl_2/hexanes to give 238 mg (80%) of **7-Te** as an orange solid, mp >250 °C. Purity was assessed by NMR spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.05 (s, 1 H), 8.52 (d, 1 H, J = 9.5 Hz), 7.87 (s, 1 H), 7.85 (d, 1 H, J = 9.5 Hz), 7.14 (dd, 1 H, J = 2.5, 9.5 Hz), 6.81 (d, 1 H, J = 2.5 Hz), 6.72 (dd, 1 H, J = 2.5, 9.0 Hz), 6.68 (d, 1 H, J = 2.0 Hz), 3.10 (s, 6 H), 3.07 (s, 6 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 185.2, 151.7, 150.1, 136.6, 134.0, 133.2, 131.0, 129.5, 127.9, 125.6, 123.6, 121.1, 116.3, 114.0, 113.1, 111.7, 102.6, 40.3, 39.9; IR (film on NaCl) 2925, 1606, 1584, 1496, 1437, 1386, 1363, 1320 cm^{-1}; HRMS (ESI, HRDFMagSec) m/z 447.0717 (calcd for $C_{21}H_{20}N_2O^{130}Te$ + H^+: 447.0711).

Extended Rhodamine 4-S. Phenylmagnesium bromide (1.0 M in THF, 2.87 mL, 2.87 mmol) was added to a stirred solution of **6-S** (100 mg, 0.297 mmol) in THF (5 mL), and the resulting mixture was heated at reflux for 16 h and then cooled to ambient temperature. The reaction was quenched by the addition of glacial acetic acid (2 mL), and the resulting mixture was poured into 100 mL of aqueous 10% HPF_6. The resulting mixture was stirred 12 h and the precipitate was collected via filtration, then washed with water (50 mL) and diethyl ether (100 mL). The crude product was recrystallized from MeOH to give 145 mg (90%) of **4-S** as a dark purple solid, mp 182−183 °C: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.49 (d, 1 H, J = 9.5 Hz), 7.64−7.71 (m, 3 H), 7.57 (d, 1 H, J = 9.0 Hz), 7.52 (d, 1 H, J = 9.0 Hz), 7.35−7.41 (m, 3 H), 7.32 (d, 1 H, J = 9.0 Hz), 7.28 (d, 1 H, J = 9.0 Hz), 7.11 (dd,

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Organometallics XXXX, XXX, XXX−XXX

1 H, J = 2.5, 9.5 Hz), 6.97 (d, 1 H, J = 2.0 Hz), 3.35 (s, 6 H), 3.25 (s, 6 H); ^{13}C NMR (75.5 MHz, CD_3CN) δ 161.3, 154.6, 154.0, 145.0, 137.5, 137.1, 136.7, 130.3, 130.0, 129.7, 129.0, 128.3, 126.9, 124.7, 121.6, 119.7, 118.5, 117.4, 110.9, 107.3, 106.6, 41.2, 40.5; λ_{max} (MeOH) 630 nm (ε = 6.1 × 10^4 M^{-1} cm^{-1}); λ_{max} (CH_2Cl_2) 641 nm (ε = 6.5 × 10^4 M^{-1} cm^{-1}); HRMS (ESI, HRDFMagSec) m/z 409.1726 (calcd for $C_{27}H_{25}N_2S^+$: 409.1733). Anal. Calcd for $C_{27}H_{25}N_2S{\cdot}PF_6$: C, 58.48; H, 4.54; N, 5.05. Found: C, 58.54; H, 4.65; N, 5.07.

Extended Rhodamine 4-Se. Phenylmagnesium bromide (1 M in THF, 1.26 mL, 1.26 mmol) and **6-Se** (50 mg, 0.126 mmol) in THF (5 mL) were treated as described for the preparation of **4-S**. The crude product was purified by recrystallization from MeOH, to give 72 mg (95%) of **4-Se** as a dark purple solid, mp 187−186 °C. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.28 (d, 1 H, J = 9.0 Hz), 7.69−7.63 (m, 3 H), 7.58 (d, 1 H, J = 10.0 Hz), 7.51 (s, 1 H), 7.45 (d, 1 H, J = 9.5 Hz), 7.37−7.33 (m, 2 H), 7.31 (d, 1 H, J = 8.5 Hz), 7.28 (d, 1 H, J = 9.0 Hz), 7.00 (d, 1 H, J = 9.5 Hz), 6.89 (s, 1 H), 3.32 (s, 6 H), 3.24 (s, 6 H); ^{13}C NMR (75.5 MHz, CD_3CN) δ 162.7, 154.1, 153.9, 147.2, 141.8, 138.7, 138.6, 137.3, 130.8, 130.1, 129.8, 129.6, 128.5, 127.8, 125.7, 122.2, 121.9, 117.5, 110.9, 109.9, 107.1, 41.3, 40.5; λ_{max} (MeOH) 647 nm (ε = 6.4 × 10^4 M^{-1} cm^{-1}); λ_{max} (CH_2Cl_2) 658 nm (ε = 6.9 × 10^4 M^{-1} cm^{-1}); HRMS (ESI, HRDFMagSec) m/z 457.1178 (calcd for $C_{27}H_{25}N_2{}^{80}Se^+$: 457.1177). Anal. Calcd for $C_{27}H_{25}N_2Se{\cdot}PF_6$: C, 53.92; H, 4.19; N, 4.66. Found: C, 54.16; H, 4.27; N, 4.63.

Extended Rhodamine 4-Te. Phenylmagnesium bromide (1 M in THF, 1.13 mL, 1.13 mmol) and **6-Te** (50 mg, 0.113 mmol) in THF (3 mL) were treated as described for the preparation of **4-S**. The crude product was purified by recrystallization from MeOH to give 67 mg (92%) of **4-Te** as a dark purple solid, mp 184−185 °C. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.93 (d, 1 H, J = 9.5 Hz), 7.78 (s, 1 H), 7.67 (d, 1 H, J = 10.0 Hz), 7.64−7.58 (m, 3 H), 7.38−7.28 (m, 4 H), 7.24 (d, 1 H, J = 9.5 Hz), 6.89 (d, 1 H, J = 9.5 Hz), 6.78 (s, 1 H), 3.27 (s, 6 H), 3.21 (s, 6 H); λ_{max} (MeOH) 666 nm (ε = 6.5 × 10^4 M^{-1} cm^{-1}); λ_{max} (CH_2Cl_2) 670 nm (ε = 6.6 × 10^4 M^{-1} cm^{-1}); HRMS (ESI, HRDFMagSec) m/z 507.1073 (calcd for $C_{27}H_{25}N_2{}^{130}Te^+$: 507.1076). Anal. Calcd for $C_{27}H_{25}N_2Te{\cdot}PF_6$: C, 49.89; H, 3.88; N, 4.31. Found: C, 50.08; H, 3.86; N, 4.21. Material was too insoluble in organic solvents for the acquisition of ^{125}Te and ^{13}C NMR spectra.

Extended Rhodamine 5-S. Phenylmagnesium bromide (1 M in THF, 2.87 mL, 2.87 mmol) and **7-S** (100 mg, 0.207 mmol) in THF (5 mL) were treated as described for preparation of **4-S**. The crude product was recrystallized from MeOH to give 145 mg (91%) of **5-S** as a dark purple solid, mp 204−205 °C. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.99 (m, 2 H), 7.67−7.70 (m, 4 H), 7.49 (d, 1 H, J = 9.5 Hz), 7.41 (dd, 2 H, J = 1.5, 8.0 Hz), 7.22 (dd, 1 H, J = 2.0, 9.0 Hz), 7.15 (d, 1 H, J = 2.0 Hz), 6.94 (dd, 1 H, J = 2.5, 9.5 Hz), 6.89 (d, 1 H, J = 2.5 Hz), 3.36 (s, 6 H), 3.25 (s, 6 H); ^{13}C NMR (75.5 MHz, CD_3CN) δ 162.5, 155.7, 153.9, 147.7, 138.8, 138.5, 138.4, 136.8, 133.9, 133.3, 133.2, 130.5, 129.7, 126.4, 123.4, 121.3, 120.5, 118.6, 117.1, 107.4, 103.0, 41.6, 40.7; λ_{max} (MeOH) 661 nm (ε = 4.71 × 10^4 M^{-1} cm^{-1}); λ_{max} (CH_2Cl_2) 689 nm (ε = 4.90 × 10^4 M^{-1} cm^{-1}); HRMS (ESI, HRDFMagSec) m/z 409.1734 (calcd for $C_{27}H_{25}N_2S^+$: 409.1733). Anal. Calcd for $C_{27}H_{25}N_2S{\cdot}PF_6$: C, 58.48; H, 4.54; N, 5.05. Found: C, 58.23; H, 4.60; N, 4.93.

Extended Rhodamine 5-Se. Phenylmagnesium bromide (1 M in THF, 2.53 mL, 1 M in THF, 2.53 mmol) and **7-Se** (100 mg, 0.253 mmol) in THF (10 mL) were treated as described for the preparation of **4-S**. The crude product was recrystallized from MeOH to give 128 mg (84%) of **5-Se** as a dark purple solid, mp 213-214 °C. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.04 (s, 1 H), 8.00 (s, 1 H), 7.72−7.60 (m, 4 H), 7.50 (d, 1 H, J = 10.0 Hz) 7.40−7.32 (m, 3 H), 7.18 (d, 1 H, J = 9.0 Hz), 6.86 (d, 1 H, J = 9.5 Hz), 6.79 (s, 1 H), 3.34 (s, 6 H), 3.24 (s, 6 H); ^{13}C NMR (75.5 MHz, CD_3CN) δ 164.0, 155.2, 154.1, 148.7, 140.6, 140.5, 138.6, 138.1, 133.6, 132.9, 130.4, 130.2, 129.6, 126.3, 124.3, 123.4, 122.2, 118.4, 116.9, 111.2, 103.1, 41.6, 40.7; λ_{max} (MeOH) 671 nm (ε = 4.71 × 10^4 M^{-1} cm^{-1}); λ_{max} (CH_2Cl_2) 700 nm (ε = 5.3 × 10^4 M^{-1} cm^{-1}); HRMS (ESI, HRDFMagSec) m/z 457.1176 (calcd for $C_{27}H_{25}N_2{}^{80}Se^+$: 457.1177). Anal. Calcd for $C_{27}H_{25}N_2Se{\cdot}PF_6$: C, 53.92; H, 4.19; N, 4.66. Found: C, 54.11; H, 4.24; N, 4.64.

Extended Rhodamine 5-Te. Phenylmagnesium bromide (1 M in THF, 1.13 mL, 1.13 mmol) and **7-Te** (50 mg, 0.113 mmol) in THF (3 mL) were treated as described for the preparation of **4-S**. The crude product was recrystallized from MeOH to give 62 mg (85%) of **5-Te** as a dark purple solid, mp 195−196 °C. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.19 (s, 1 H), 8.09 (s, 1 H), 7.68−7.60 (m, 3 H), 7.59−7.57 (m, 3 H), 7.34−7.36 (m, 2 H), 7.13 (d, 1 H, J = 9.5 Hz), 6.77 (d, 1 H, J = 9.0 Hz), 6.73 (s, 1 H), 3.29 (s, 6 H), 3.22 (s, 6 H); λ_{max} (MeOH) 623 nm (ε = 4.89 × 10^4 M^{-1} cm^{-1}); λ_{max} (CH_2Cl_2) 633 nm (ε = 5.0 × 10^4 M^{-1} cm^{-1}); HRMS (ESI, HRDFMagSec) m/z 507.1082 (calcd for $C_{27}H_{25}N_2{}^{130}Te^+$: 507.1076). Anal. Calcd for $C_{27}H_{25}N_2Te{\cdot}PF_6$: C, 49.89; H, 3.88; N, 4.31. Found: C, 49.83; H, 3.93; N, 4.16. Material was too insoluble in organic solvents for the acquisition of ^{125}Te and ^{13}C NMR spectra.

Fluorescence Experiments. Measurements of fluorescence quantum yields for the **4-E** and **5-E** dyes were performed on a spectrofluorometer using fluorescent dye LD 700 perchlorate (Rhodamine 700) as a reference with known Φ_{FL} = 0.38[38] in MeOH. Each dye as well as the reference was excited at 600 nm with an absorbance of 0.10 at 600 nm for the chromophore.

Determination of Singlet Oxygen Yields from Singlet Oxygen Luminescence Spectroscopy. Generation of $^1O_2$ was assessed by its luminescence peak at 1270 nm. Time-resolved detection of the long-lived $^1O_2$ emission was used to distinguish signal from $^1O_2$ as previously described.[36] The second harmonic (532 nm) from a nanosecond pulsed Nd:YAG laser operating at 20 Hz was used as the excitation source. Additional long-pass filters were used to attenuate the scattered light and fluorescence from the samples. The samples (methanol solutions of the compounds in quarts cuvettes) were placed in front of the spectrometer entrance slit.

Computational Details. Calculations were done with Gaussian09,[39] and input files and results were visualized using GaussView05.[40] All structures were optimized using the B3LYP[41−43] level of theory with the 6-311+G(d)[44−49] basis set for all light atoms and LanL2DZ for Te. TD-DFT[50] calculations were performed from the optimized geometries. The UV−vis spectra were modeled with 0.17 eV fwhm Gaussians on each transition.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00255.

Text and figures giving general methods and NMR spectral data (^{1}H and ^{13}C NMR) for all noncommercial compounds; ^{1}H NMR spectra for the mixtures of regioisomers from **11a** with *sec*-BuLi/TMEDA and **8-E**; TD-DFT-calculated absorption spectra; and time-resolved singlet-oxygen emission spectra (PDF)

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Author Contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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Organometallics XXXX, XXX, XXX−XXX

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Organometallics XXXX, XXX, XXX−XXX