# **Supplementary Information**

# Polycyclic arene-fused selenophenes via site selective selenocyclization of arylethynyl substituted polycyclic arenes

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#### Effect of additional water on product formation.

2-(4-(tert-butyl)phenyl)naphtho[1,2-b]selenophene (2c) and (E)-2-(4-(tert-butyl)styryl)-naphthalene (2ca).



Four sets of reactions were put in four 15 ml volume capacity sealed tubes (pressure tube) containing **1c** (95 mg, 0.34 mmol) and selenium powder (221 mg, 2.66 mmol) in dry NMP (1.2 ml) in each with different percentage of additional water and simultaneously refluxed at 205 °C for 78 h using a single oil bath.

Set 1. - 1.2 ml NMP + 1% distilled water

Set 2. -1.2 ml NMP +2% distilled water

Set 3. – 1.2 ml NMP + 3% distilled water

Set 4. - 2 ml NMP + 15% distilled water

It was observed that with increase in water percentage in the reaction mixture fraction of *E*-alkene is increased with respect to the fused selenophene but total yield of the product was decreased gradually. But adding 2 ml of NMP with 15% (v/v) water to the reaction mixture no product was formed, rather it gave the starting material back (Figure S44).

2-(4-(tert-butyl)phenyl)phenanthro[9,10-b]selenophene (2a) and (E)-9-(4-(tert-butyl)-styryl)phenanthrene (2aa)



Reaction between **1a** (100 mg, 0.30 mmol) and selenium powder (190 mg, 2.4 mmol) was carried out in dry NMP (2 ml) in a sealed tube in presence of additional 2% of water (2.22 Tmmol). The trans-alkene **2aa** corresponding to **1a** was obtained in major quantity (87%) in mixture with **2a** (Figure S45). The mixture of **2a** and **2aa** is not separable using simple column chromatography. After fractional crystallization of 50 mg of product mixture from DCM/Hexane (1:20) solvent mixture (20 ml) at room temperature white needle shaped crystals of **2aa** (30 mg) was obtained after 24 h. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 8.75 (d, *J* = 7.8, 1H), 8.67 (d, *J* = 7.9, 1H), 8.26 (d, *J* = 7.8, 1H), 7.96 (s, 1H), 7.92 (d, *J* = 7.3, 1H), 7.84 (d, *J* = 15.9, 1H), 7.72 – 7.56 (m, 6H), 7.45 (d, *J* = 8.4, 2H), 7.26 (s, CDCl<sub>3</sub>) 7.22 (d, *J*=15.9, 1H), 1.55 (s, H<sub>2</sub>O), 1.38 (s, 9H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 151.2, 135.0, 134.4, 132.1, 131.0, 130.6, 130.3, 128.8, 128.3, 127.5, 127.0, 126.8, 126.7, 126.2, 125.9, 125.8, 124.9, 124.6,

123.7, 123.3, 122.7, 34.9, 31.5. HRMS (ESI-TOF) m/z  $[M+H]^+$  calcd for  $C_{26}H_{25}$  337.1950, found 337.1949.

# **Recycling of Selenium powder.**

The selenium powder was used during the formation of fused selenophene is immiscible with NMP and can be reused after purification. Also, no significant change in powder XRD data of selenium powder was found after the reaction from its initial state (Figure S1).<sup>1</sup> It signifies that there is no chemical change that occurred during the reaction in selenium powder. Only the crystallinity of selenium powder was improved during reaction, which was indicated by the sharpening of peaks of respective positions (Figure S1).



Figure S1. PXRD data of selenium powder (i) initially (ii) after first cycle and (iii) after Third cycle

## **Experimental details**

## First Cycle

To verify the reusability of selenium powder, **1a** (112 mg, 0.334 mmol) and Se (210 mg; 2.67 *m*mol.) was taken in a 15 ml Schlenk tube containing a magnetic stirrer bar. The system was degassed and refilled with nitrogen, and dry NMP (1.2 ml) was added. The temperature of the system was slowly raised to 205 °C and kept constant for a further 48 h. After cooling to room temperature DCM (10 ml) was added to dilute the mixture and collected using a glass syringe after allowing to settled remaining selenium powder for 15 min. The process was repeated 2-3 times until the solution becomes clear, and the sealed tube containing unreacted selenium powder was dried in an oven. The liquid part was treated with NH<sub>4</sub>Cl and washed with 2 x 100 ml of water to remove NMP. The product mixture was collected in DCM and dried over Na<sub>2</sub>SO<sub>4</sub> to concentrated under reduced pressure. Residual NMP was removed from the product mixture by performing flash column chromatography on silica gel (100-200) packed column

using Hexane/DCM solvent mixture (50:1) to obtain 118 mg crude solid. It was observed from <sup>1</sup>H NMR analysis (Figure S47(a)) that 63% of the starting material was converted to product **2a**, and the remaining 37% starting material remain as such.

# Second Cycle

Unreacted selenium powder obtained after the first cycle was weighed (183 mg, 2.32 mmol) and reused for the second cycle. It was reacted with **1a** (97 mg, 0.290 mmol) in the presence of NMP (1 ml) following the same procedure employed in the first cycle by maintaining exactly the same substrate to selenium ratio (1:8). After workup total of 96 mg of crude solid was obtained containing the majority of **2a** (59%) and the rest is **1a** (41%) as observed in their <sup>1</sup>H NMR data (Figure S47(b)).

# Third Cycle

After the second cycle remaining selenium powder (160 mg, 2.02 mmol) was reacted with **1a** (84 mg, 0.253 mmol) in the presence of NMP (1 ml), yielding 78 mg of crude solid. This time corresponding *E*-alkene **2aa** (20%) was obtained along with fused selenophene **2a** (40%) and unreacted starting material **1a** (40%) (Figure S47(c)).

Tab	Table S1 Recycling of selenium powder								
		Substrate	colonium	NIMD	Isolated N	Aixture after Re	eaction*		
	Cycles	( <b>1a</b> ) mg (mmol)	mg (mmol)	INIVIE	Substrate (1a)%	Selenophene (2a)%	Alkene (2aa)%		
	1	112 (0.334)	210 (2.67)	1.2 ml	63	37	-		
	2	97 (0.290)	183 (2.32)	1 ml	59	41	-		
	3	84 (0.253)	160 (2.02)	1 ml	40	40	20		

\* percentage yield determined using NMR spectra



Figure S2. Yield of product formation at different cycles.

# Single Crystal X-ray Diffraction Study.

All the crystals were obtained by the slow evaporation method from the mixture of solvents at room temperature. After the formation of good quality crystals, they are generally kept under ethanol as an anti-solvent. For diffraction, a suitable crystal was chosen from a glass slide covered with mineral oil. The crystals were diffracted on Super Nova, Dual, Cu/Mo at zero,

Eos diffractometer. The crystals were solved using Olex2,<sup>2</sup> the structure was solved with the ShelXT<sup>3</sup> structure solution program and refined with the ShelXL<sup>4</sup> refinement package using Least Squares minimization. Details of crystal data were listed in Table S1.

Identification code	2a	2c	2ea	2 <b>g</b>
Empirical formula	$C_{26}H_{22}Se$	C22H20Se	C24H16	$C_{26}H_{16}Se$
Formula weight	413.40	363.34	304.37	407.35
Temperature/K	100.00	100.00(10)	100	100.00
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$I_2$	P21	P21	$\mathbf{P}_{bca}$
a/Ă	19.253(2)	7.9313(3)	12.7769(9)	9.58910(10)
b/Å	6.0322(4)	11.3299(4)	4.0491(2)	14.4311(2)
c/Å	18.774(2)	18.9666(7)	15.6492(10)	25.6817(3)
$\alpha/^{\circ}$	90.00	90.00	90.00	90.00
β/°	118.999(15)	91.108(3)	107.939(7)	90.00
$\gamma/^{\circ}$	90.00	90.00	90.00	90.00
Volume/Å <sup>3</sup>	1907.0(4)	1704.04(11)	770.25(8)	3553.87(7)
Z	4	4	2	8
$\rho_{calc}g/cm^3$	1.440	1.416	1.312	1.523
$\mu/\text{mm}^{-1}$	2.696	2.201	0.074	2.892
F(000)	848.0	744.0	320.0	1648.0
Crystal size/mm <sup>3</sup>	$\begin{array}{c} 0.08 \times 0.06 \times \\ 0.04 \end{array}$	$\begin{array}{c} 0.5\times 0.2\times \\ 0.1\end{array}$	$\begin{array}{c} 0.09\times 0.03\times \\ 0.01\end{array}$	$\begin{array}{c} 0.05\times 0.05\times \\ 0.01\end{array}$
Radiation	Cu Kα (λ = 1.54184)	Mo K $\alpha$ ( $\lambda = 0.71073$ )	Mo K $\alpha$ ( $\lambda = 0.71073$ )	CuK $\alpha$ ( $\lambda = 1.54184$ )
20 range for data collection/°	9.16 to 131.1	4.18 to 50.04	3.36 to 49.98	6.88 to 132.34
Index ranges	$\begin{array}{c} -22 \leq h \leq 22, -\\ 7 \leq k \leq 5, -21\\ \leq l \leq 22 \end{array}$	$\begin{array}{c} -9 \leq h \leq 9,  -7 \\ \leq k \leq 13,  -22 \\ \leq 1 \leq 22 \end{array}$	$\begin{array}{c} \text{-15} \leq h \leq \text{15, -} \\ 4 \leq k \leq 4,  \text{-18} \\ \leq 1 \leq 18 \end{array}$	$-11 \le h \le 11, -17 \le k \le 16, -30 \le 1 \le 30$
Reflections collected	6302	7623	5353	32979
Independent reflections	$\begin{array}{l} 2571 \; [R_{int} = \\ 0.0525, \\ R_{sigma} = \\ 0.0537] \end{array}$	4300 [Rint = 0.0308, Rsigma = 0.0514]	2623 [Rint = 0.0212, Rsigma = 0.0300]	$\begin{array}{l} 3102 \; [R_{int} = \\ 0.0510, \\ R_{sigma} = \\ 0.0216] \end{array}$
Data/restraints/parameters	2571/1/248	4300/1/421	2623/1/217	3102/0/244
Goodness-of-fit on F <sup>2</sup>	1.048	1.069	1.293	1.068
Final R indexes [I>=2σ (I)]	$\begin{array}{l} R_1 = 0.0603, \\ wR_2 = 0.1521 \end{array}$	R1 = 0.0379, wR2 = 0.0892	R1 = 0.0519, wR2 = 0.1594	$\begin{array}{l} R_1 = 0.0384, \\ wR_2 = 0.0955 \end{array}$
Final R indexes [all data]	$\begin{array}{l} R_1 = 0.0618, \\ wR_2 = 0.1542 \end{array}$	R1 = 0.0430, wR2 = 0.0920	R1 = 0.0603, wR2 = 0.1643	$\begin{array}{l} R_1 = 0.0413, \\ wR_2 = 0.0977 \end{array}$
Largest diff. peak/hole / e $\text{\AA}^{-3}$	1.73/-1.21	0.74/-0.40	0.14/-0.22	1.62/-0.51
Flack parameter	-0.03(4)	0.044(12)	3(10)	
Identification code	2041369	2041373	2042639	2042641

Table S2. Crystal data and structure refinement

Identification code	2ha	2i	2kb
Empirical formula	C28H18	C17H16Se	$C_{34}H_{32}$
Formula weight	354.42	299.26	440.60
Temperature/K	293(2)	100.00(10)	293(2)
Crystal system	monoclinic	triclinic	triclinic
Space group	$C_c$	P-1	P-1
a/Å	32.303(5)	6.1989(5)	9.8772(5)
b/Å	6.2174(12)	11.0621(10)	13.1988(5)
c/Ă	9.0416(19)	20.7731(19)	21.2332(9)
$\alpha/\circ$	90.00	104.826(8)	92.631(3)
β/°	97.505(16)	98.430(7)	98.313(4)
$\gamma/^{\circ}$	90.00	92.099(7)	107.660(4)
Volume/Å3	1800.4(6)	1358.1(2)	2598.1(2)
Z	4	4	4
pcalcg/cm3	1.308	1.464	1.126
μ/mm-1	0.562	2.744	0.063
F(000)	744.0	608.0	944.0
Crystal size/mm3	$\begin{array}{c} 0.08\times 0.03\times \\ 0.01\end{array}$	$\begin{array}{c} 0.56 \times 0.42 \times \\ 0.25 \end{array}$	$\begin{array}{c} 0.08 \times 0.03 \times \\ 0.01 \end{array}$
Radiation	Cu Kα (λ = 1.54184)	Mo Kα (λ = 0.71073)	Μο Κα (λ = 0.71073)
20 range for data collection/°	5.52 to 132.02	3.82 to 54.94	6.34 to 50.58
Index ranges	$-38 \le h \le 37, -7 \le k \le 6, -10 \le 1 \le 10$	$\begin{array}{c} -8 \leq h \leq 5, -9 \\ \leq k \leq 14, -25 \\ \leq 1 \leq 23 \end{array}$	$-11 \le h \le 11, -15 \le k \le 15, -25 \le 1 \le 25$
Reflections collected	3316	3776	49023
Independent reflections	2164 [Rint = 0.0334	3328 [Rint =	9443 [ $R_{int} = 0.0527$
	Rsigma =	Rsigma =	$R_{sigma} =$
	0.0487]	0.0447]	0.0423]
Data/restraints/parameters	2164/2/253	3328/0/181	9443/0/625
Goodness-of-fit on F2	1.037	1.030	1.026
Final R indexes [I>=2σ (I)]	R1 = 0.0802, wR2 = 0.2116	R1 = 0.0440, wR2 = 0.1057	$R_1 = 0.0631,$ $wR_2 = 0.1656$
Final R indexes [all data]	R1 = 0.0878, wR2 = 0.2256	R1 = 0.0574, wR2 = 0.1145	$R_1 = 0.1220,$ $wR_2 = 0.2009$
Largest diff. peak/hole / e Å-3	0.51/-0.25	0.77/-0.50	0.34/-0.23
Flack parameter	-5(4)		
Identification code	2041466	2042640	2047804

We have found that the large flack parameter (3(10)) was associated with the crystal **2ea**, which is most probably due to the presence of twinning nature in the crystal which was believed to cause the inversion of the structure (as observed during changing the thermal ellipsoids to anisotropy while solving the crystal in Olex2) via changing the coordinates.

The diffraction measured fraction theta full value for the crystal **2i** was found as 0.622, which is lower than the expected value. The reason for this error may be the crystals obtained for **2i** were found to be twinned with a severe overlap of Bragg reflections from both domains. Data reduction was performed for both domains, while a significant number of reflections were rejected due to bad agreement between reflection profiles (mostly partially overlapped) in order to obtain a reasonable structural model.



Figure S3. ORTEP of 2a with 50% probability (Hydrogens are omitted for clarity).



Figure S4. ORTEP of 2c with 50% probability (Hydrogens are omitted for clarity).



Figure S5. ORTEP of 2ea with 50% probability (Hydrogens are omitted for clarity).



Figure S6. ORTEP of 2g with 50% probability (Hydrogens are omitted for clarity).



Figure S7. ORTEP of **2ha** with 50% probability (Hydrogens are omitted for clarity).



Figure S8. ORTEP of 2i with 50% probability (Hydrogens are omitted for clarity).



Figure S9. ORTEP of 2k with 50% probability (Hydrogens are omitted for clarity).

#### **Optical Study.**

Experimental details of UV-vis absorption and fluorescence spectroscopy.

The UV-vis absorption and fluorescence spectra of the compounds were recorded in solution state by dissolving them in chloroform at the concentration of  $10^{-5}$  M on Perkin Elemer Lamba 35 UV-Vis spectrometer. Fluorescence spectra of the same were recorded on Horiba JobinYvon, Fluoromax-3 (Xe-150 W, 250-900 nm). Most of the compounds absorbed light in UV region (340-390 nm) except for pyrene based compounds, which shows absorption maxima at the visible region (beyond 400 nm). All of them emits mainly in the blue region. The only pyrene based trans-alkenes **2fa** and **2ha** emit in the green region, which is also observed under UV light (335 nm). The relative fluorescence quantum yield ( $\Phi_F$ ) of the fluorophores were calculated against the standard solution of Quinine sulfate in 0.1 M H<sub>2</sub>SO<sub>4</sub>, which give  $\Phi_F =$ 0.57 when excited at 350 nm. For this purpose, the solutions were diluted to  $10^{-6}$  M concentration range to restrict the absorbance of each compound under 0.1, which maintain a proper balance between absorption and emission during the calculation of  $\Phi_F$ . The emission spectra for all the fluorophores were recorded by exciting each of them at 350 nm. The  $\Phi_F$ values of the fluorophores were calculated from the following equation (eqn. 1).

$$\Phi_F = \Phi_{QS} X \frac{(Intigrated FL Intensity)Fluorophore}{(Intigrated FL Intensity)Qs} X \frac{(O.D.)Qs}{(O.D.)Fluorophores} X (\frac{\eta_{CHCl_3}}{\eta_{H_2O}})^2 \dots eqn. S1$$

Where  $\Phi_{Qs}$  is the fluorescence quantum yield of quinine sulfate;  $\eta_{CHCl_3}$  and  $\eta_{H_2O}$  are the refractive indices of CHCl<sub>3</sub> and H<sub>2</sub>O, respectively (refractive index of 0.1 M H<sub>2</sub>SO<sub>4</sub> is similar to water).



Figure S10. UV absorption spectra of 2c

# Quantitative analysis of HOMO coefficient.

The HOMO coefficients of **1b**, **1g**, **1n** and **1o** was calculated from their optimized structure via DFT calculation at B3LYP/6-31G(d) using multiwfn program.<sup>6</sup> Individual HOMO coefficient of each atom is given in Table S3.

	Orbital 76		24 25 25 28 30 30 30 30 30 30 30 30 30 30 30 30 30		Orbital68		Orbital64
10,	HOMO		HOMO		HOMO	10, 1	HOMO
Atom	coefficient	Atom	coefficient	Atom	coefficient	Atom	coefficient
1	8.027	1	0.965	1	7.346	1	8.087
2	1.67	2	3.415	2	1.431	2	1.732
3	2.14	3	2.92	3	1.999	3	2.153
4	8.622	4	3.515	4	7.114	4	9.03
5	4.618	5	1.543	5	3.35	5	5.081
6	0.412	6	4.755	6	0.315	6	0.446
7	3.906	7	9.524	7	3.117	7	4.145
8	2.432	8	0.946	8	1.766	8	2.675
9	4.947	9	0.874	9	3.689	9	5.394
10	0.577	10	6.842	10	0.533	10	0.579
11	0.301	11	2.12	11	0.243	11	0.317

Table S3. HOMO coefficient of different atoms for 1b, 1g, 1n and 1o.

12	0.169	12	0.224	12	0.122	12	0.186
13	0.369	13	0.79	13	0.275	13	0.401
14	9.933	14	1.69	14	10.705	14	9.425
15	11.65	15	1.543	15	10.711	15	11.508
16	4.709	16	0.68	16	6.432	16	4.33
17	3.511	17	0.044	17	3.378	17	3.531
18	1.659	18	0.247	18	2.848	18	1.586
19	0.241	19	0.096	19	0.217	19	0.247
20	5.632	20	0.396	20	6.163	20	4.828
21	0.083	21	0.05	21	0.183	21	0.092
22	10.784	22	0.135	22	9.371	22	11.109
23	0.845	23	0.117	23	0.743	23	0.867
24	4.414	24	8.965	24	3.59	24	4.678
25	0.288	25	9.156	25	0.228	25	0.308
26	4.072	26	6.039	26	4.576	26	3.535
27	0.287	27	1.7	27	0.315	27	0.248
28	1.672	28	6.229	28	2.893	28	1.575
29	0.092	29	2.857	29	0.211	29	0.091
30	0.627	30	1.214	30	5.054	30	1.816
31	0.415	31	3.065	31	0.501		
32	0.031	32	0.451	32	0.275		
33	0.106	33	2.653	33	0.032		
34	0.055	34	0.268	34	0.275		
35	0.415	35	3.147				
36	0.055	36	7.958				
37	0.106	37	0.195				
38	0.031	38	1.498				
39	0.057	39	0.207				
40	0.019	40	0.234				
41	0.019	41	0.63				
42	0.003	42	0.103				

The electronic states involved during the desired electronic transition of **2aS**, **2aSe**, **2dS** and **2dSe** were determined via TD-DFT calculation at B3LYP/6-31G. The HOMO coefficients of different atoms of those compounds were calculated using multiwfn program<sup>6</sup> at the ground states of those particular transitions. The individual HOMO coefficient of each atom is given in Table S4.

Table S4. Molecular Orbital dia	gram at ground	l states of	2aS, 2	2aSe,	2dS	and	2dSe	for
different electronic transitions.								

<b>2aS</b> , Orbital 96	<b>2aS</b> , Orbital 97	2aSe, Orbital 105	<b>2aSe</b> , Orbital 106
HOMO-1	HOMO	HOMO-1	HOMO

	HOMO		HOMO		HOMO		HOMO
Atom	coefficient	Atom	coefficient	Atom	coefficient	Atom	coefficient
1	2.456	1	12.562	1	24.315	1	2.764
2	12.887	2	2.703	2	0.274	2	4.208
3	1.565	3	11.006	3	2.177	3	10.913
4	6.164	4	6.268	4	4.071	4	3.78
5	0.46	5	0.432	5	9.041	5	1.498
6	2.726	6	8.528	6	8.193	6	6.209
7	10.164	7	1.23	7	0.615	7	0.433
8	1.893	8	3.298	8	9.117	8	1.284
9	0.072	9	0.273	9	2.45	9	4.658
10	8.534	10	1.088	10	0.256	10	0.343
11	0.662	11	0.065	11	0.172	11	4.842
12	5.974	12	2.826	12	6.426	12	1.089
13	0.437	13	0.227	13	0.493	13	0.065
14	2.706	14	2.362	14	4.342	14	4.467
15	0.124	15	0.179	15	0.174	15	3.638
16	10.85	16	1.441	16	0.159	16	0.269
17	5.509	17	4.541	17	0.181	17	3.204
18	6.194	18	2.163	18	0.044	18	0.257
19	0.428	19	0.138	19	1.957	19	2.391
20	1.543	20	6.437	20	0.08	20	0.18
21	0.065	21	0.534	21	3.261	21	8.872
22	8.121	22	1.312	22	1.193	22	6.346
23	0.643	23	0.059	23	0.055	23	0.526
24	4.128	24	4.697	24	3.956	24	2.164
25	0.346	25	0.342	25	0.268	25	0.139
26	4.212	26	3.909	26	5.676	26	2.938
27	0.247	27	4.272	27	0.427	27	0.236
28	0.19	28	3.724	28	0.036	28	1.405
29	0.036	29	0.297	29	0.002	29	0.075
30	0.039	30	1.444	30	2.241	30	12.571
31	0.002	31	0.084	31	5.86	31	1.283
32	0.18	32	4.893	32	0.467	32	0.058
33	0.152	33	1.49	33	1.727	33	3.384
34	0.011	34	0.082	34	0.07	34	0.281
35	0.118	35	3.186	35	0.15	35	1.486
36	0.085	36	0.228	36	0.012	36	0.089
37	0.023	37	0.543	37	0.023	37	0.537
38	0.013	38	0.351	38	0.017	38	0.35
39	0.002	39	0.048	39	0.002	39	0.047
40	0.003	40	0.087	40	0.001	40	0.025
41	0.001	41	0.026	41	0.005	41	0.088
42	0.018	42	0.368	42	0.008	42	0.356
43	0.002	43	0.048	43	0.001	43	0.093
44	0.002	44	0.029	44	0	44	0.028

45	0.006	45	0.097	45	0.002	45	0.047
46	0.002	46	0.05	46	0.003	46	0.051
47	0.001	47	0.017	47	0	47	0.003
48	0	48	0.015	48	0.001	48	0.016
49	0	49	0.003	49	0.001	49	0.018

3 30 73 10 40 32 73 10 40 30 10 40 30 10 40 30 10 40 30 10 40 30 10 40 40 10		3 3 23 6 2 6 3 23 7 9 4 3 7 2 7 9 4 3 7 2 1 8 1 3 7 2 1 8		3 21 <sup>22</sup> 3 31 <sup>21</sup> 10 3 <sup>34</sup> 22 0 <sup>32</sup> 22	
20	<b>IS</b> , Orbital102 HOMO-1	2d8	6, Orbital 103 HOMO	2dSe, Orbital 112 HOMO	
			HOMO		HOMO
Atom	HOMO coefficient	Atom	coefficient	Atom	coefficient
1	5.202	1	7.086	1	6.949
2	12.362	2	3.219	2	3.157
3	3.24	3	2.322	3	2.228
4	2.143	4	6.962	4	7.228
5	0.915	5	0.217	5	0.218
6	7.603	6	2.122	6	2.098
7	1.745	7	2.017	7	1.839
8	2.107	8	2.025	8	9.792
9	0.851	9	9.832	9	2.103
10	9.007	10	2.026	10	0.776
11	1.405	11	0.803	11	0.164
12	0.156	12	0.154	12	0.741
13	0.987	13	0.785	13	0.149
14	0.19	14	0.163	14	3.895
15	2.063	15	4.018	15	7.017
16	3.265	16	6.875	16	0.443
17	2.263	17	0.432	17	2.635
18	3.357	18	2.716	18	0.045
19	0.092	19	0.047	19	0.039
20	0.054	20	0.045	20	8.729
21	1.901	21	8.764	21	0.963
22	6.846	22	0.999	22	1.582
23	5.057	23	1.553	23	0.575
24	0.189	24	0.563	24	2.835
25	1.313	25	2.802	25	0.289
26	0.478	26	0.357	26	2.09
27	3.481	27	2.109	27	0.685
28	0.177	28	0.684	28	2.709
29	3.452	29	2.692	29	6.39
30	7.772	30	6.223	30	0.074
31	0.369	31	0.073	31	3.571

32	4.643	32	3.534	32	9.395
33	0.414	33	0.284	33	0.095
34	0.093	34	0.067	34	3.882
35	0.092	35	0.078	35	0.503
36	0.714	36	9.46	36	0.262
37	0.272	37	0.096	37	0.753
38	2.37	38	3.847	38	0.287
39	0.582	39	0.489	39	0.185
40	0.339	40	0.259	40	0.025
41	0.099	41	0.061	41	0.013
42	0.034	42	0.026	42	0.046
43	0.038	43	0.028	43	0.191
44	0.027	44	0.759	44	0.05
45	0.16	45	0.283	45	0.015
46	0.043	46	0.024	46	0.026
47	0.006	47	0.004	47	0.027
48	0.006	48	0.004	48	0.008
49	0.003	49	0.002	49	0.009
50	0.021	50	0.012	50	0.002
51	0.003	51	0.002	51	2.216

NMR spectra of Products (2a-n):



Figure S11. (i)  ${}^{1}$ H (400 MHz, CDCl<sub>3</sub>) and (ii)  ${}^{13}$ C{ ${}^{1}$ H} (125 MHz, CDCl<sub>3</sub>) NMR Spectra of **2a** 









Figure S12. (i) <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and (ii) <sup>2</sup>H (77 MHz, CHCl<sub>3</sub>) NMR Spectra of deuterated product **2a-1D** and (iii) Comparison of <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) spectra of **2a** and **2a-1D** 





Figure S13. (i) <sup>1</sup>H (500 MHz, CDCl<sub>3</sub>), (ii) <sup>13</sup>C{<sup>1</sup>H} (125 MHz, CDCl<sub>3</sub>) and (iii) <sup>77</sup>Se{<sup>1</sup>H}(95 MHz, CDCl<sub>3</sub>) NMR Spectra of **2b** 



Figure S14. (i)  ${}^{1}$ H (400 MHz, CDCl<sub>3</sub>) and (ii)  ${}^{13}$ C{ ${}^{1}$ H} (100 MHz, CDCl<sub>3</sub>) NMR Spectra of **2c** 



Figure S15. (i) <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and (ii) <sup>77</sup>Se{<sup>1</sup>H} (95 MHz, CDCl<sub>3</sub>) NMR Spectra of mixture of **2c** and **2ca** 





-538.4

Figure S16. (i) <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>), (ii) <sup>13</sup>C{<sup>1</sup>H} (125 MHz, CDCl<sub>3</sub>) and (iii) <sup>77</sup>Se{<sup>1</sup>H} (95 MHz, CDCl<sub>3</sub>) NMR Spectra of 2d



(iii)

#### -138.0 132.1 132.1 132.1 132.1 132.1 133.1 133.1 133.1 133.1 122.5 1225.5 1255.



Figure S17. (i)  ${}^{1}$ H (400 MHz, CDCl<sub>3</sub>) and (ii)  ${}^{13}$ C{ ${}^{1}$ H} (100 MHz, CDCl<sub>3</sub>) NMR Spectra of

2ea





Figure S18. (i) <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and (ii) <sup>13</sup>C{<sup>1</sup>H} (100 MHz, CDCl<sub>3</sub>) NMR Spectra of 2fa





Figure S19. (i) <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and (ii) <sup>2</sup>H (77 MHz, CHCl<sub>3</sub>) NMR Spectra of **2fa-2D** and (iii) Comparison of <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) of **2f** and **2fa** 



Figure S20. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) NMR Spectra of (i) product mixture (**1g+2g**) (1:2) and (ii) pure **2g**.



Figure S21.  ${}^{1}$ H (400 MHz, CDCl<sub>3</sub>) and  ${}^{13}$ C{ ${}^{1}$ H} (100 MHz, CDCl<sub>3</sub>) NMR Spectra of **2ha** 



Figure S22. (i)  ${}^{1}$ H (400 MHz, CDCl<sub>3</sub>) and (ii)  ${}^{13}$ C{ ${}^{1}$ H} (125 MHz, CDCl<sub>3</sub>) NMR Spectra of **2i** 



Figure S23. (i)  ${}^{1}$ H (400 MHz, CDCl<sub>3</sub>) and (ii)  ${}^{13}$ C{ ${}^{1}$ H} (100 MHz, CDCl<sub>3</sub>) NMR Spectra of **2ja** 



Figure S24. (i) <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and (ii) <sup>13</sup>C{<sup>1</sup>H} (100 MHz, CDCl<sub>3</sub>) NMR Spectra of 2kb



Figure S25. (i)  ${}^{1}$ H (400 MHz, CDCl<sub>3</sub>) and (ii)  ${}^{13}$ C{ ${}^{1}$ H} (100 MHz, CDCl<sub>3</sub>) NMR Spectra of **2**I





Figure S27. (i)  ${}^{1}$ H (400 MHz, CDCl<sub>3</sub>) and (ii)  ${}^{13}$ C{ ${}^{1}$ H} (100 MHz, CDCl<sub>3</sub>) NMR Spectra of **2n** 

8.37 8.37 98.35 7.91 7.91 7.16

(i)

-1.57







Figure S28. (i) <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>), (ii) <sup>13</sup>C{<sup>1</sup>H} (100 MHz, CDCl<sub>3</sub>) and (iii) <sup>19</sup>F{<sup>1</sup>H} (375 MHz, CDCl<sub>3</sub>) NMR Spectra of **20** 



# NMR spectra of arylethynyl substituted polyarenes (1a-n).







Figure S32. (i)  ${}^{1}$ H (400 MHz, CDCl<sub>3</sub>) and (ii)  ${}^{13}$ C{ ${}^{1}$ H} (100 MHz, CDCl<sub>3</sub>) NMR Spectra of **1d** 





#### S39











Figure S36. (i)  ${}^{1}$ H (400 MHz, CDCl<sub>3</sub>) and (ii)  ${}^{13}$ C{ ${}^{1}$ H} (100 MHz, CDCl<sub>3</sub>) NMR Spectra of **1i** 





(ii)

Figure S37. (i)  ${}^{1}$ H (400 MHz, CDCl<sub>3</sub>) and (ii)  ${}^{13}$ C{ ${}^{1}$ H} (100 MHz, CDCl<sub>3</sub>) NMR Spectra of 1j





S43



Figure S39.  $^{1}$ H (400 MHz, CDCl<sub>3</sub>) and  $^{13}$ C{ $^{1}$ H} (100 MHz, CDCl<sub>3</sub>) NMR Spectra of **1**I



Figure S40. (i)  ${}^{1}$ H (400 MHz, CDCl<sub>3</sub>) and (ii)  ${}^{13}$ C{ ${}^{1}$ H} (100 MHz, CDCl<sub>3</sub>) NMR Spectra of **1m** 



Figure S42. <sup>1</sup>H NMR Spectra (400 MHz, CDCl<sub>3</sub>) of 10





Figure S43. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) NMR Spectra obtained during selenocyclization of **1c** in 1.2 ml of (a) 1% (b) 2% (c) 3% (v/v) water in NMP and (d) 2 ml of 15% (v/v) water in NMP



#### S49



2aa

(i)

L7.99 L7.96 L7.89



L7.99 L7.96 77.87 (ii) 1 ~7.99 7.89 1a 1.4 2a 8.0 7.9 f1 (ppm) 1 1 0.0 2.5 9.5 9.0 8.5 8.0 7.5 7.0 6.0 5.5 5.0 4.5 f1 (ppm) 3.5 3.0 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 6.5 4.0 7.99 7.91 7.93 7.91 7.87 (iii) 1 1a -7.99 ~7.91 1 2a 0.5 ġ 2aa 8.01 7.92 f1 (ppm) 1.0 5.0 4.5 4.0 f1 (ppm) 5.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0



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