## **Supporting Information**

# Simultaneous enhancement of transition dipole strength and vibrational lifetime of an alkyne IR probe *via* $\pi$ -d backbonding and vibrational decoupling

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#### SI. Syntheses of compounds

General. <sup>1</sup>H and <sup>13</sup>C spectra were recorded on a Bruker Ascend 500 NMR spectrometer. Chemical shifts ( $\delta$ ) and coupling constants (J) are reported in parts per million (ppm) and hertz (Hz), respectively. <sup>1</sup>H NMR spectra are referenced to TMS (0.05% v/v tetramethylsilane in CDCl<sub>3</sub>) as an internal standard. <sup>13</sup>C NMR spectra are referenced to solvent (<sup>13</sup>C: CDCl<sub>3</sub>,  $\delta$  77.00 ppm) as an internal standard. High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-700 mass spectrometer using an electron impact (EI) technique. Thin-layer chromatography (TLC) was performed on silica gel 60 F<sub>254</sub> precoated plates (0.25 mm thickness, Merck, Darmstadt). Flash chromatography was carried out on silica gel 60 (230–400 mesh, Merck). Reagent-grade chemicals were purchased from Aldrich and TCI and used as received unless otherwise specified.

**PhSCCTMS (2).**<sup>S1</sup> To a cooled (-78 °C) and stirred solution of ethynyltrimethylsilane (495 mg, 712 µL, 5.04 mmol) in distilled THF (20 mL) under Ar was added *n*-butyllithium solution (2.5 M in hexanes, 2.02 mL, 5.05 mmol) dropwise over 1 min. After stirring under Ar at -78 °C for 30 min, a solution of diphenyl disulfide 7 (1.0 g, 4.58 mmol) in distilled THF (10 mL) was added dropwise over 5 min. After stirring under Ar at room temperature for 1 h, the reaction mixture was quenched with H<sub>2</sub>O (50 mL) and extracted with Et<sub>2</sub>O (50 mL × 2). The combined organic layers were washed with 1 N aqueous NaOH (10 mL × 3) and brine (20 mL), dried over MgSO<sub>4</sub>, and concentrated *in vacuo*. The residue was purified by flash chromatography (*n*-hexane) to give **2** (840 mg, 89%) as a pale yellow oil. TLC (*n*-hexane)  $R_f = 0.56$ ; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.41 (dd, J = 8.5, 1.5 Hz, 2H), 7.34 (t, J = 7.8 Hz, 2H), 7.22 (tt, J = 7.3, 1.5 Hz, 1H), 0.25 (s, 9H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  132.31, 129.21, 126.50, 126.10, 106.33, 90.08, -0.11; HRMS (EI+) for C<sub>11</sub>H<sub>14</sub>SSi ( $M^+$ ), calcd 206.0586, found 206.0586.

**PhSCCH (5).**<sup>S1</sup> To a cooled (0 °C) and stirred solution of **2** (840 mg, 4.08 mmol) in MeOH (10 mL) was added potassium carbonate (675 mg, 4.88 mmol). After strring at room temperature for 2 h, the reaction mixture was quenched with H<sub>2</sub>O (10 mL) and extracted with Et<sub>2</sub>O (20 mL × 2). The combined organic layers were washed with brine (10 mL), dried over MgSO<sub>4</sub>, and concentrated *in vacuo*. The residue was purified by flash chromatography (*n*-hexane) to give **5** 

(496 mg, 91%) as a brown oil. TLC (*n*-hexane)  $R_f = 0.53$ ; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.45 (dd, J = 8.8, 1.3 Hz, 2H), 7.35 (t, J = 7.8 Hz, 2H), 7.24 (tt, J = 7.4, 1.3 Hz, 1H), 3.25 (s, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  131.49, 129.28, 126.81, 126.59, 86.87, 71.03; HRMS (EI+) for C<sub>8</sub>H<sub>6</sub>S ( $M^+$ ), calcd 134.0190, found 134.0188.

**PhSeCCTMS (3).** To a cooled (-78 °C) and stirred solution of ethynyltrimethylsilane (346 mg, 498 μL, 3.52 mmol) in distilled THF (20 mL) under Ar was added *n*-butyllithium solution (2.5 M in hexanes, 1.41 mL, 3.53 mmol) dropwise over 1 min. After stirring under Ar at -78 °C for 30 min, a solution of diphenyl diselenide **8** (1.0 g, 3.20 mmol) in distilled THF (10 mL) was added dropwise over 5 min. After stirring under Ar at room temperature for 1 h, the reaction mixture was quenched with H<sub>2</sub>O (50 mL) and extracted with Et<sub>2</sub>O (50 mL × 2). The combined organic layers were washed with 1 N aqueous NaOH (10 mL × 3) and brine (20 mL), dried over MgSO<sub>4</sub>, and concentrated *in vacuo*. The residue was purified by flash chromatography (*n*-hexane) to give **3** (623 mg, 77%) as a yellow oil. TLC (*n*-hexane)  $R_f = 0.54$ ; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.51 (dd, J = 8.3, 1.3 Hz, 2H), 7.32 (t, J = 7.3 Hz, 2H), 7.25 (tt, J = 7.4, 1.3 Hz, 1H), 0.24 (s, 9H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  129.50, 128.79, 128.41, 127.00, 111.62, 84.27, -0.07; HRMS (EI+) for C<sub>11</sub>H<sub>14</sub>SeSi (*M*<sup>+</sup>), calcd 254.0030, found 254.0028.

**PhSeCCH (6).** To a cooled (0 °C) and stirred solution of **3** (623 mg, 2.45 mmol) in MeOH (10 mL) was added potassium carbonate (408 mg, 2.95 mmol). After strring at room temperature for 2 h, the reaction mixture was quenched with H<sub>2</sub>O (10 mL) and extracted with Et<sub>2</sub>O (20 mL × 2). The combined organic layers were washed with brine (10 mL), dried over MgSO<sub>4</sub>, and concentrated *in vacuo*. The residue was purified by flash chromatography (*n*-hexane) to give **6** (252 mg, 57%) as a yellow/brown oil. TLC (*n*-hexane)  $R_f = 0.53$ ; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.55 (dd, J = 8.3, 1.3 Hz, 2H), 7.33 (t, J = 7.3 Hz, 2H), 7.28 (tt, J = 7.3, 1.4 Hz, 1H), 3.18 (s, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  129.57, 129.42, 127.42, 127.35, 91.49, 64.50; HRMS (EI+) for C<sub>8</sub>H<sub>6</sub>Se ( $M^+$ ), calcd 181.9635, found 181.9635.

## SII. FTIR spectral analyses

Solvent	Peak 1		Peak 2	
	$\omega_0$	FWHM	$\omega_0$	FWHM
DMSO	2156.4	10.8		
DMF	2157.5	9.8		
CHCl <sub>3</sub>	2157.5	13.0		
THF	2159.2	8.5		
MeOAc	2159.1	8.5		
МеОН	2159.7	9.4		
TFE	2150.9	12.4	2160.6	11.5
Hexane	2161.7	8.2		
Heptane	2162.2	7.9		

Table S1 Fitting results for the FTIR spectra of 1 in various solvents<sup>a</sup>

<sup>*a*</sup> Parameters obtained from Voigt fitting to FTIR spectra in Fig. 2b.  $\omega_0$  and FWHM in cm<sup>-1</sup>.

Solvent	Peak 1		Peak 2	
	$\omega_0$	FWHM	$\omega_0$	FWHM
DMSO	2094.5	13.0		
DMF	2095.4	12.0		
CHCl <sub>3</sub>	2095.3	15.9		
THF	2096.5	10.5		
MeOAc	2096.8	11.5		
МеОН	2097.2	11.2		
TFE	2087.0	14.5	2098.3	13.0
Hexane	2098.4	11.1		
Heptane	2098.9	10.3		

 Table S2 Fitting results for the FTIR spectra of 2 in various solvents<sup>a</sup>

<sup>*a*</sup> Parameters obtained from Voigt fitting to FTIR spectra in Fig. 2c.  $\omega_0$  and FWHM in cm<sup>-1</sup>.

Solvent	Peak 1		Peak 2	
	$\omega_0$	FWHM	$\omega_0$	FWHM
DMSO	2087.9	13.6		
DMF	2089.0	12.6		
CHCl <sub>3</sub>	2089.6	15.5		
THF	2090.6	11.5		
MeOAc	2090.9	11.0		
МеОН	2091.2	11.9		
TFE	2080.4	13.6	2091.6	13.9
Hexane	2093.1	11.2		
Heptane	2093.4	10.5		

Table S3 Fitting results for the FTIR spectra of 3 in various solvents<sup>a</sup>

<sup>*a*</sup> Parameters obtained from Voigt fitting to FTIR spectra in Fig. 2d.  $\omega_0$  and FWHM in cm<sup>-1</sup>.

#### SIII. Solvatochromic analyses



Fig. S1 Plot of the C=C stretch frequencies against the dielectric constant  $\varepsilon$  (a) and Kamlet–Taft parameters  $\alpha$  (b) and  $\beta$  (c) of the solvents used here for 1–3. Among the solvents having  $\alpha = \beta = 0$ , only DMSO and hexane are chosen to be shown in (b) and (c), respectively. Fitted constants: (a) 1 ( $R^2 = 0.45$ , slope = -0.08), 2 ( $R^2 = 0.42$ , slope = -0.06), 3 ( $R^2 = 0.53$ , slope = -0.08); (b) 1 ( $R^2 = 0.97$ , slope = 2.73), 2 ( $R^2 = 0.99$ , slope = 2.47), 3 ( $R^2 = 0.87$ , slope = 2.25); (c) 1 ( $R^2 = 0.29$ , slope = -3.16), 2 ( $R^2 = 0.25$ , slope = -2.20), 3 ( $R^2 = 0.39$ , slope = -3.51).

#### SIV. Calculation details



**Fig. S2** Model molecules used for natural bond orbital analyses with their specific atom numbering. H-atom numbering is omitted for clarity unless otherwise indicated. Model molecules are (a) PhCCTMS, (b) PhSCCTMS, (c) PhSeCCTMS, (d) PhCCH, (e) PhSCCH, and (f) PhSeCCH.

	Donor NBO (i)	Acceptor NBO (j)	E(2) (kcal/mol)	$E_{\rm j} - E_{\rm i}$ (a.u.)	F(i,j) (a.u.)
	BD (2) C7-C8	RY*(2) Si9	0.55	1.38	0.025
	BD (2) C7–C8	BD*(1) C1–C2	3.50	0.83	0.048
	BD (2) C7–C8	BD*(1) C1–C6	3.50	0.83	0.048
PhCCTMS	BD (2) C7–C8	BD*(1) Si9–C10	0.65	0.54	0.017
	BD (2) C7–C8	BD*(1) Si9–C11	2.59	0.54	0.034
	BD (2) C7–C8	BD*(1) Si9–C12	0.65	0.54	0.017
	BD (3) C7–C8	RY*(3) C1	1 37	1 17	0.037
	BD (3) C7-C8	RV*(1) Si9	0.57	134	0.025
	BD (3) C7–C8	BD*(2) C1_C6	11 44	0.30	0.057
	BD (3) C7 C8	BD*(1) Si0_C10	1 01	0.50	0.037
	BD(3)C7 = C8	$DD^{*}(1) Si9-C10$	1.91	0.54	0.029
	BD (3) C7-C8	BD*(1) S19-C12	1.91	0.54	0.029
	BD (2) C8–C9	$RY^{*}(2)S/$	2.56	0.81	0.041
	BD (2) C8-C9	RY*(1) Si10	0.62	1.32	0.026
	BD (2) C8–C9	BD*(2) C8–C9	0.73	0.39	0.015
	BD (2) C8–C9	BD*(1) Si10-C11	1.93	0.55	0.029
PhSCCTMS	BD (2) C8–C9	BD*(1) Si10-C12	1.93	0.55	0.029
TIBCCTWB	BD (3) C8–C9	RY*(1) S7	2.02	1.07	0.042
	BD (3) C8–C9	BD*(1) C1-S7	3.88	0.47	0.038
	BD (3) C8–C9	BD*(1) Si10-C11	0.52	0.56	0.015
	BD (3) C8–C9	BD*(1) Si10-C12	0.52	0.56	0.015
	BD (3) C8–C9	BD*(1) Si10-C13	1.93	0.56	0.029
	BD (2) C8–C9	RY*(2) Se7	1.76	0.78	0.033
	BD (2) C8-C9	RY*(1) Si10	0.62	1.30	0.026
	BD (2) C8–C9	BD*(2) C8–C9	0.61	0.39	0.014
	BD (2) C8–C9	BD*(1) Si10-C11	1.85	0.55	0.029
PhSaCCTMS	BD (2) C8–C9	BD*(1) Si10-C13	1.85	0.55	0.029
	BD (3) C8–C9	RY*(1) Se7	1.11	1.04	0.030
	BD (3) C8–C9	BD*(1) C1–Se7	3.37	0.41	0.033
	BD (3) C8–C9	BD*(1) Si10–C11	0.52	0.56	0.015
	BD (3) C8–C9	BD*(1) Si10–C12	1.94	0.56	0.029
	BD (3) C8-C9	$BD^{*}(1) S110-C13$ BV*(2) C1	0.52	0.56	0.015
	BD (2) C7-C8	$\frac{RT}{2}CI$	0.32	1.82	0.028
	BD (2) C7-C8	$BD^{*}(1) C1 - C2$	3.47	0.84	0.048
РһССН	BD (2) C7-C8	BD*(1) C1-C6	3.44	0.84	0.048
	BD (2) C7–C8	BD*(1) C5–C6	1.30	1.37	0.038
	BD (2) C7–C8	BD*(1) C8–H9	1.65	5.75	0.087
	BD (3) C7–C8	RY*(4) C1	1.48	1.11	0.037
	BD (3) C7–C8	BD*(2) C1–C2	10.82	0.31	0.057
PL C C C L	BD (2) C8–C9	RY*(2) S7	2.63	0.79	0.041
PhSCCH	BD (3) C8–C9	RY*(1) S7	2.04	1.09	0.042
	BD (3) C8–C9	BD*(1) C1–S7	3.76	0.48	0.038
	BD (2) C8–C9	KY*(1) Se7	1.79	0.72	0.032
PhSeCCH	BD (3) C8–C9	KY*(2) Se7	1.12	1.06	0.031
	BD (3) C8–C9	BD*(1) C1–Se7	3.26	0.42	0.033

**Table S4** Stabilization energies of the delocalization interaction between donor and acceptorNBOs in model molecules<sup>a</sup>

<sup>*a*</sup> The stabilization energy, E(2), of the delocalization interaction between donor NBO (*i*) and acceptor NBO (*j*) is estimated as

$$E(2) = q_i \frac{F(i,j)^2}{E_j - E_i}$$
(1)

where  $q_i$  is the occupancy of the donor orbital,  $E_i$  and  $E_j$  are the energies of the donor and acceptor orbitals, and F(i, j) is the interaction (Fock matrix) element between donor and acceptor orbitals. The NBO label gives the type (BD for 2-center bond, RY\* for 1-center Rydberg, and BD\* for 2-center antibond), a serial number in parenthesis (1, 2, 3,..., for the same type of bonds), the atom(s) to which the NBO is affixed (see Fig. S2 of the ESI† for the numbering of the atoms in the six molecules). Note that the E(2) values listed here are only for most of the C=C  $\pi$  donor orbitals. The  $\pi$ -d backbondings between BD (2) C7–C8 ( $\pi_x$ ) and RY\* (2) Si9 ( $d_{xz}$ ) and between BD (3) C7–C8 ( $\pi_y$ ) and RY\* (1) Si9 ( $d_{yz}$ ) in 1 are shown in Fig. 3.

### SV. IR pump-probe data analyses



Fig. S3 Time- and frequency-resolved isotropic IR pump–probe signals at the delay time t for 1–3 (a–c) in CHCl<sub>3</sub> after background corrections to raw spectra.

	Probe frequency (cm <sup>-1</sup> )	<i>y</i> <sub>0</sub> (a.u.)	$A_{1}$ (a.u.)	<i>T</i> <sub>1</sub> (ps)
1	2160.0	$8.43 \times 10^{-5} \pm 3.65 \times 10^{-5}$	$3.22 \times 10^{-3} \pm 6.01 \times 10^{-5}$	$5.68\pm0.29$
2	2095.5	$-6.79 \times 10^{-4} \pm 1.21 \times 10^{-4}$	$8.78 \times 10^{-3} \pm 1.62 \times 10^{-4}$	$11.36 \pm 0.64$
3	2097.2	$3.09 \times 10^{-4} \pm 8.04 \times 10^{-5}$	$2.75 \times 10^{-3} \pm 7.68 \times 10^{-5}$	94.13 ± 5.91

**Table S5** Fitting results of the vibrational population decays of 1-3 in CHCl<sub>3</sub><sup>*a*</sup>

<sup>*a*</sup> Parameters obtained from fitting vibrational population decays (see Fig. 4a of the main text) to a single-exponential decay function.  $A_1$  is the amplitude,  $T_1$  is the vibrational lifetime, and  $y_0$  is an offset of a fitting curve.

## References

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