Supporting Information

Exceptional Ultrafast Nonlinear Optical Response of Functionalized Silicon Nanosheets

Michalis Stavrou, [‡a,b] Amelie M. Mühlbach, [‡c] Vasilios Arapakis, [a,b] Elisabeth Groß, [c] Tim Kratky, [d] Sebastian Günther, [d] Bernhard Rieger, *[c] and Stelios Couris *[a,b]

[a]*Department of Physics, University of Patras, 265 04 Patras, Greece.*
E-mail: couris@upatras.gr

[b]*Foundation for Research and Technology Hellas-Institute of Chemical Engineering Sciences (FORTH/ICE-HT), 26504 Rio-Patras, Greece.*
E-mail: couris@iceht.forth.gr

[c] *Wacker-Chair of Macromolecular Chemistry, Department of Chemistry, TUM School of Natural Sciences, Technical University of Munich, Lichtenbergstraße 4, 85748 Garching, Germany.*
E-mail: rieger@tum.de

[d] *Physical Chemistry with Focus on Catalysis, Department of Chemistry, TUM School of Natural Sciences, Technical University of Munich, Lichtenbergstraße 4, 85748 Garching, Germany.*

‡ These authors contributed equally

FT-IR and Raman spectra

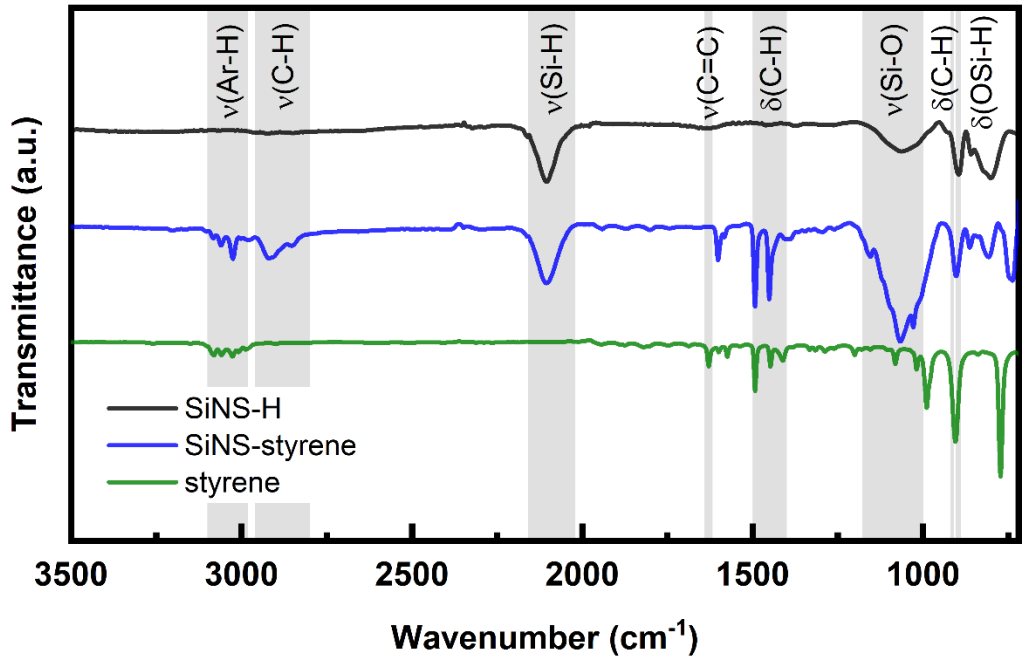

Figure S1. FT-IR spectra of SiNS-H, SiNS-styrene, and styrene (ν: stretching, δ: deformation vibrations).

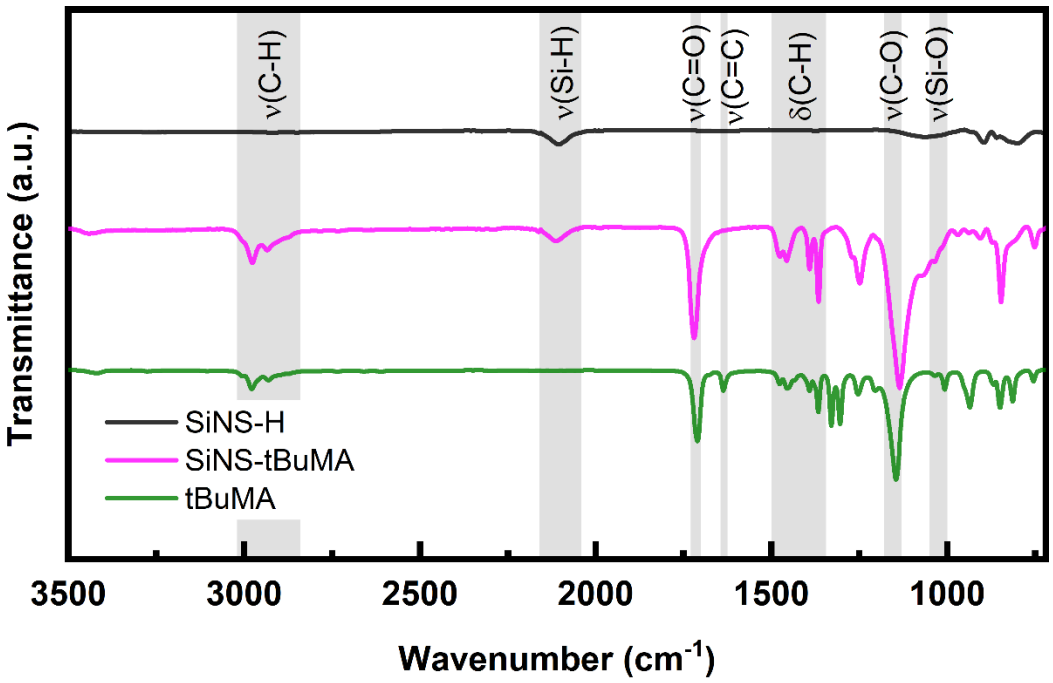

Figure S2. FT-IR spectra of SiNS-H, SiNS-tBuMA, and tBuMA (ν: stretching, δ: deformation vibrations).

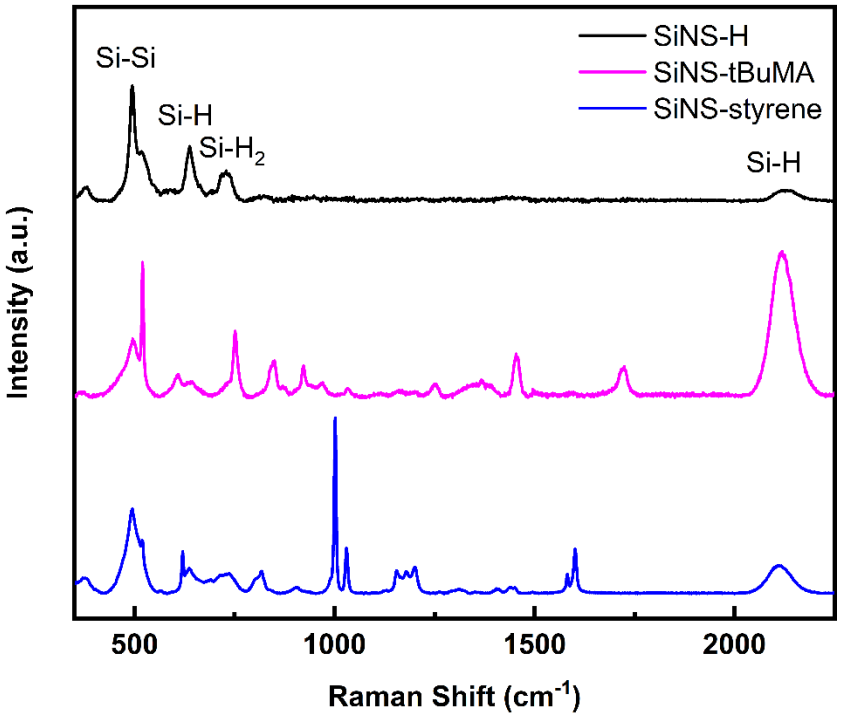

Figure S3. Raman spectra of SiNS-H, SiNS-styrene, and SiNS-tBuMA.

TGA measurements

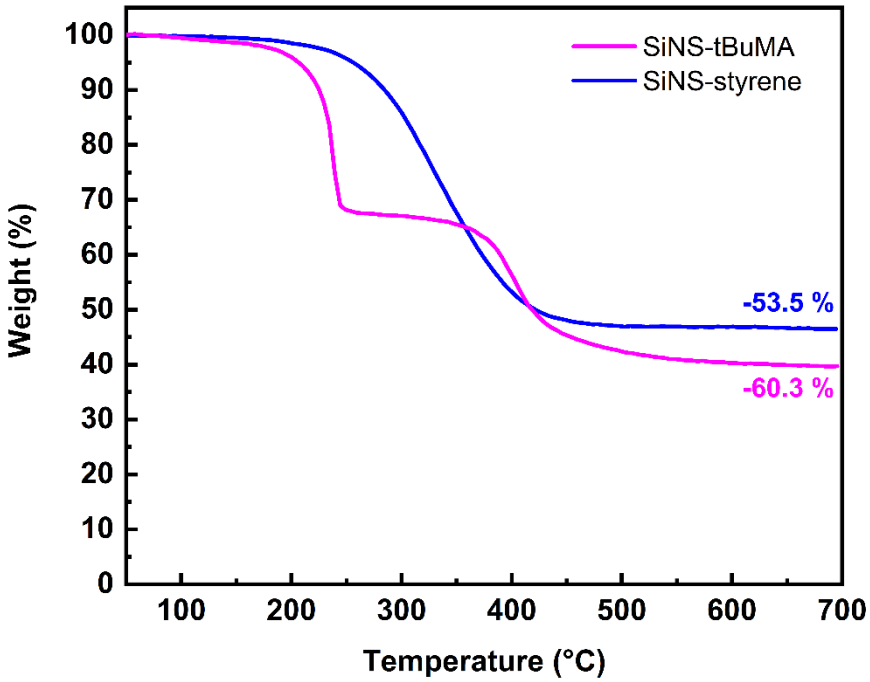

Figure S4. TGA data of SiNS-styrene and SiNS-tBuMA.

Surface coverage

Assuming that the mass loss obtained from TGA is only due to the cleavage of styrene or tBuMA, respectively, and the remaining mass is silicon, the surface coverages of functionalized SiNSs were calculated by the ratio of the amount of organic groups to the amount of silicon (equation (S1)):

$$\frac{n_R}{n_{Si}} = \frac{M_{Si}}{M_R} \cdot \frac{ML}{1-ML} \quad \text{(S1)}$$

where n_R is the amount of either styrene or tBuMA, n_{Si} is the amount of silicon, ML is the mass loss, M_R is the molar mass of styrene (104.2 g/mol) or tBuMA (142.2 g/mol), and M_{Si} is the molar mass of silicon (28.09 g/mol). Protons attached to silicon are neglected in this calculation. Table S1 shows the TGA mass losses and corresponding surface coverages of the functionalized SiNSs calculated with equation (S1).

Table S1. TGA mass loss and calculated surface coverages of functionalized SiNSs.

	TGA mass loss	**surface coverage**
SiNS-styrene	54%	31%
SiNS-tBuMA	60%	30%

AFM images

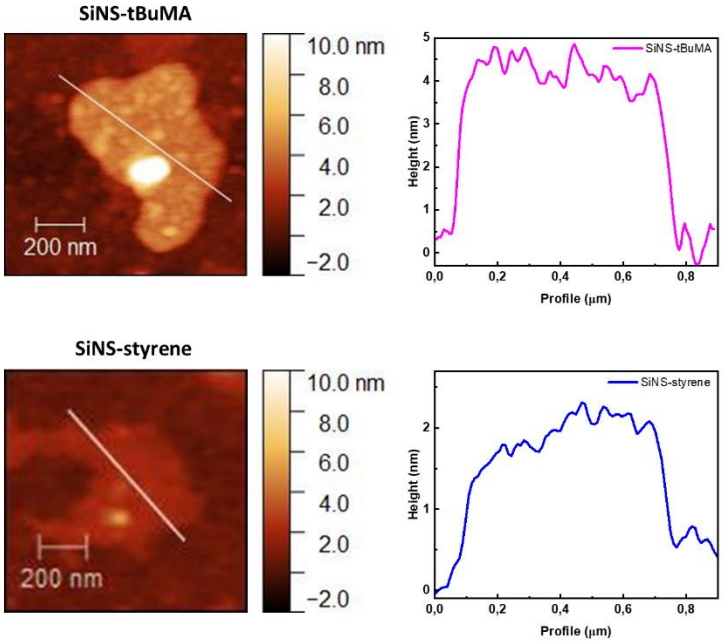

Figure S5. AFM images of SiNS-tBuMA and SiNS-styrene.

Electron microscopy images

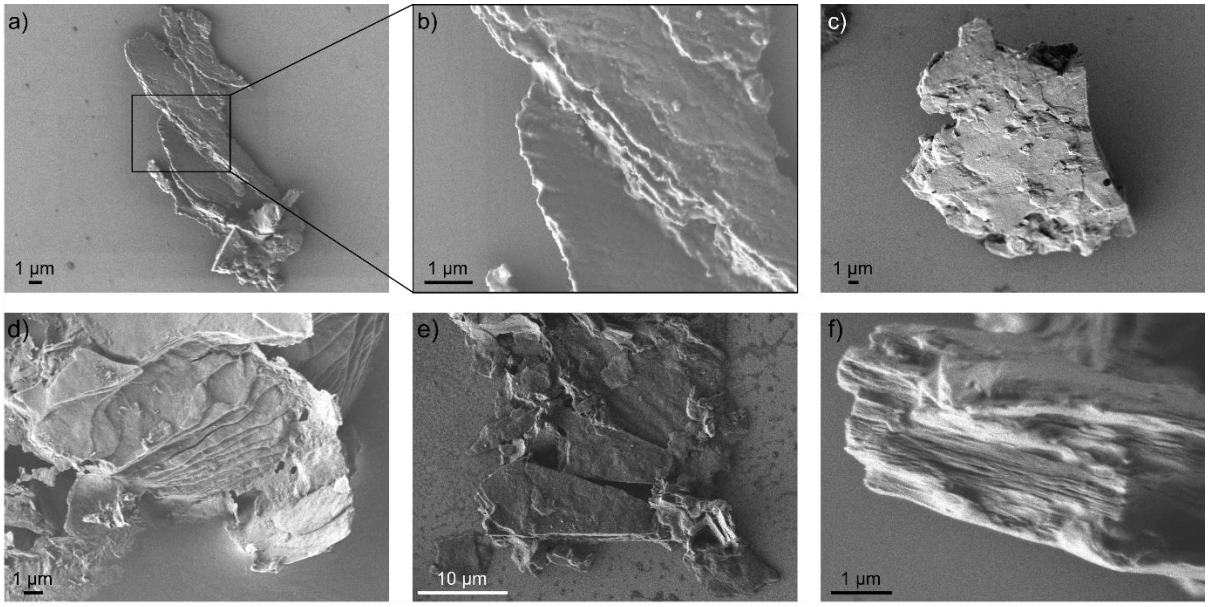

Figure S6. SEM images of SiNS-styrene (a-c) and SiNS-tBuMA (d-f). a), c), and e) show some dark spots beside the nanosheets, indicating residual polymer.

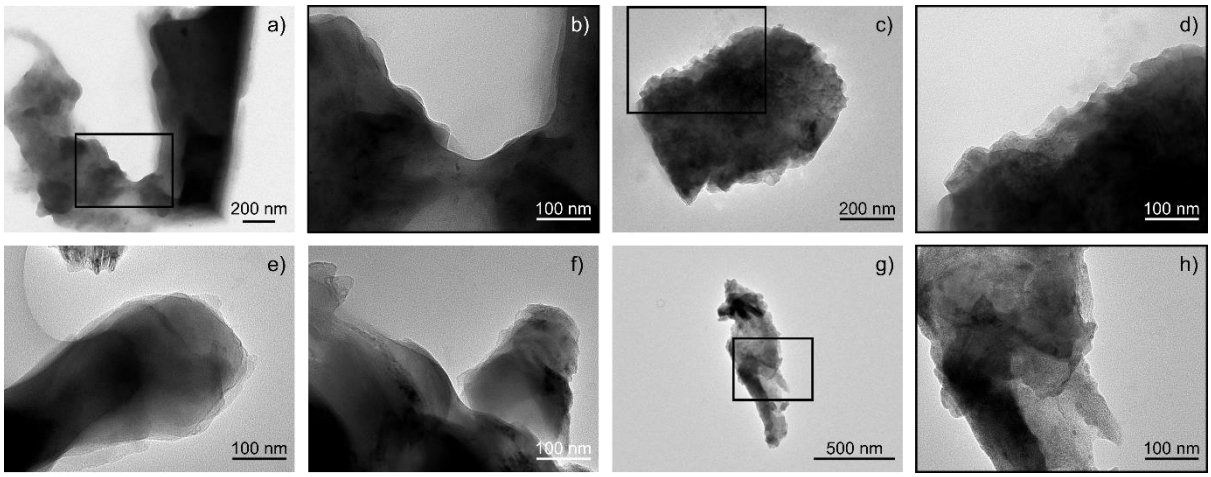

Figure S7. TEM images of SiNS-styrene (a-d) and SiNS-tBuMA (e-h). b), c), and h) show higher magnifications of a), c), and g), respectively.

PL spectra

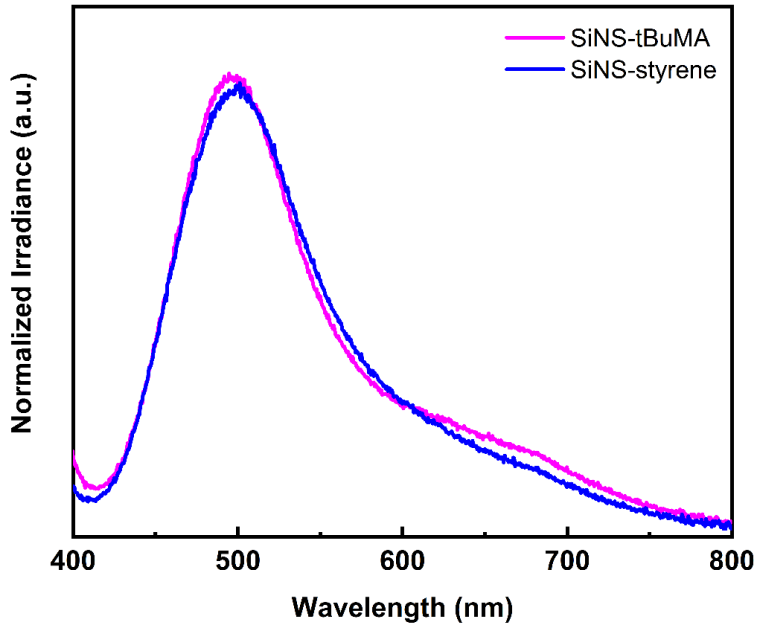

Figure S8. PL spectra of SiNSs functionalized with styrene and tBuMA, excited at 365 nm.

Both PL spectra exhibit an emission maximum at 500 nm, independent of their surface group. This is a typical value for SiNS capped with organic groups.[S1]

Intensity-dependent nonlinear absorption coefficient

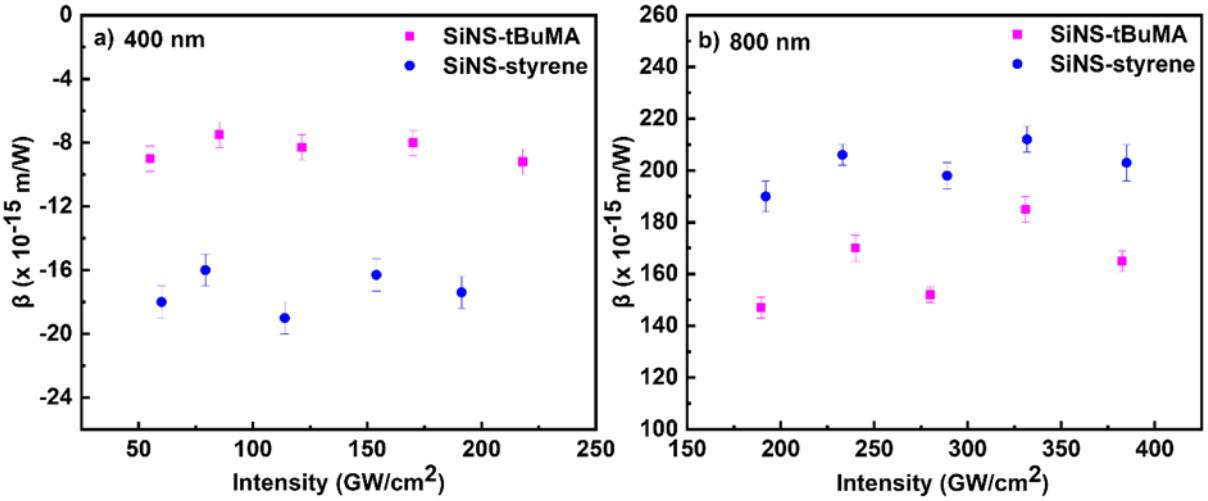

Figure S9. Intensity-independent nonlinear absorption coefficient β of SiNS-tBuMA and SiNS-styrene under (a) 400 and (b) 800 nm laser excitation. All the values refer to a concentration of 0.1 mg/mL.

Z-scan recordings of SiNS-H

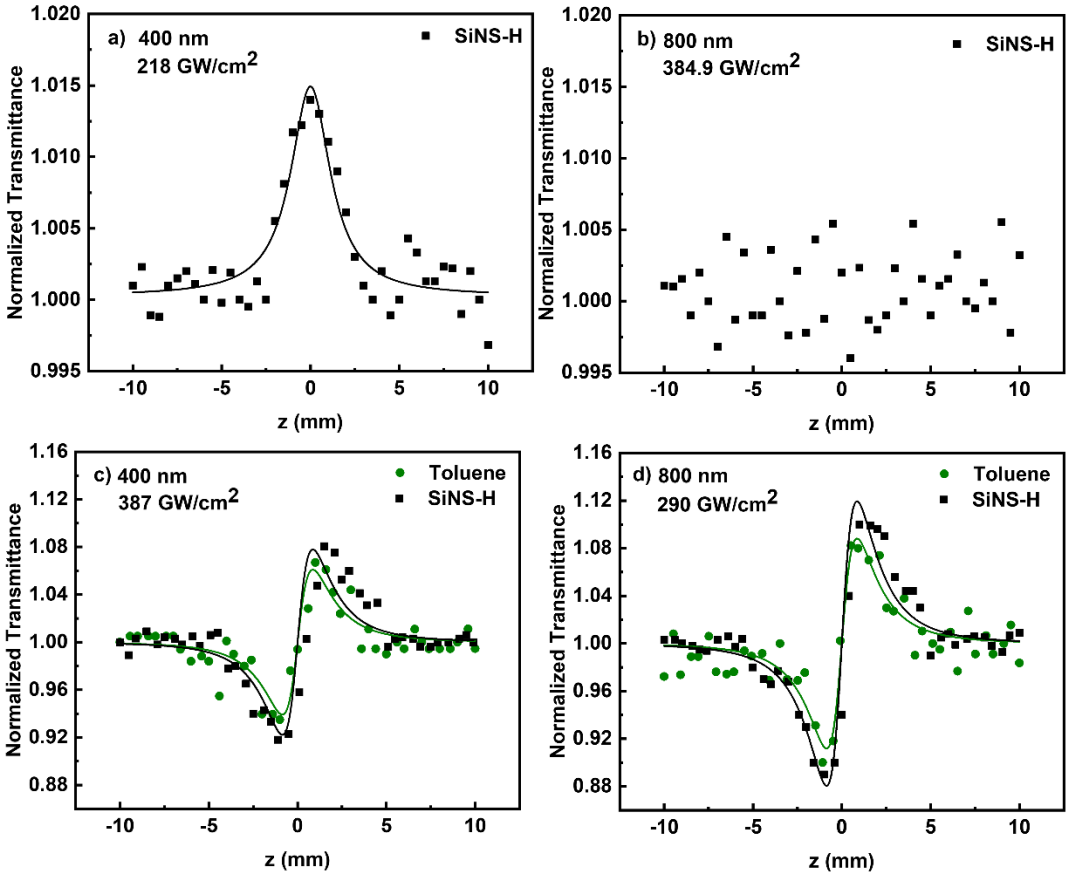

Figure S10. OA (a, b) and "divided" Z-scans (c, d) of SiNS-H under fs, 400 and 800 nm laser excitation. All the Z-scans refer to a concentration of 1 mg/mL.

Purity of SiNS-styrene and SiNS-tBuMA

To determine whether the samples of functionalized SiNSs only consist of SiNSs covalently bonded to styrene or tBuMA moieties or a composite material of surface functionalized SiNSs embedded in a polymer matrix, two experiments were performed: In the first experiment, SiNS-styrene and SiNS-tBuMA dispersions in THF (6.7 mg/mL) were sonicated for 9 hours. The supernatant was filtered through a 0.45µm syringe filter and analyzed *via* GPC with a refractive index detector. The chromatograms showed no signals to be assigned to polymeric or oligomeric structures. This result was further confirmed by thin layer chromatography (TLC). Therefore, dispersions of SiNS-styrene and SiNS-tBuMA in DCM (5.0 mg/mL) were sonicated for 7 hours. After sedimentation of the SiNSs, small spots of the supernatants were applied to a silica plate. The TLC plate was developed in THF, dried, and visualized under UV light. As no spots appeared for the SiNS samples, it was concluded that the functionalized SiNSs are

pure samples without any impurities (remaining initiating iodonium salt or monomers) or polymer matrix. Minor traces of polymeric structures were observed in SEM images (Figure S6a), c), and e)), but as GPC experiments did not detect polymer in the samples, the low concentration of residual polymer is probably negligible.

NLO properties of SiNS-tBuMA, SiNS-styrene, and other 2D nanomaterials

Table S2. NLO absorption-related parameters (β: nonlinear absorption coefficient; $Im\chi^{(3)}$: imaginary part of the third-order susceptibility; FOM: figure of merit (i.e., $Im\chi^{(3)}/\alpha_0$)) of SiNS-tBuMA, SiNS-styrene, and other 2D nanostructures, all measured under similar laser excitation conditions at 800 nm.

Excitation conditions	**Sample**	**T (%)**	**α_0 (cm^{-1})**	**β ($\times 10^{-15}$ m/W)**	**$Im\chi^{(3)}$ ($\times 10^{-16}$ esu)**	**FOM ($\times 10^{-16}$ esu cm)**	**Ref.**
130 fs, 800 nm, 10 Hz	GO/water	~90	0.52	30	13.5	26	S1
100 fs, 800 nm, 1 KHz	Reduced-GO/glass	~78	6.7×10^4	336×10^4	1.94×10^{-8}	2895	S2
100 fs, 800 nm, 100 kHz	$Ti_3C_2T_x$ (large flakes)/water	-	9.6	120 ± 22	214	34.9	S3
	$Ti_3C_2T_x$ (small flakes)/water	-	16.2	89 ± 20	158	19.7	
100 fs, 800 nm, 1 kHz	NbS_2	-	8.2	2.1	1.0	0.12	S4
35 fs, 800 nm, 1 kHz	1L-WS_2/Sapphire	-	1.53×10^6	1183×10^4	3.53×10^{-8}	230	S5
	10L-WS_2/Sapphire	-	1.83×10^5	192×10^4	0.57×10^{-8}	310	
	1L-MoS_2/Sapphire	-	3.16×10^5	1018×10^4	3.49×10^{-8}	1110	
	13L-MoS_2/ Sapphire	-	5.20×10^4	144×10^4	0.49×10^{-8}	940	
70 fs, 800 nm, 10Hz	SiNS-styrene	90	1.0	203	115.8	115.8	this work
	SiNS-tBuMA			164.7	93.9	93.9	

Table S3. Saturable absorption-related parameters (β: nonlinear absorption coefficient; $Im\chi^{(3)}$: imaginary part of the third-order susceptibility; FOM: figure of merit (i.e., $Im\chi^{(3)}/\alpha_0$); α_s: modulation depth; I_s: saturable intensity) of SiNS-styrene, SiNS-tBuMA, and other 2D nanostructures.

Sample	**Excitation conditions**	**T (%)**	**α_0 (cm^{-1})**	**β ($\times 10^{-15}$ m/W)**	**$Im\chi^{(3)}$ ($\times 10^{-16}$ esu)**	**FOM ($\times 10^{-16}$ esu cm)**	**α_s (%)**	**I_s (GW/cm^2)**	**Ref.**
SiNS-styrene	50 fs, 400 nm, 10 Hz	79	2.55	-8.3	-2.5	1.0	20	255	this work
SiNS-tBuMA				-17	-5	2.0	17	620	
Graphene/CHP	100 fs, 800 nm, 1 kHz	16.8	17.85	-152	-87	4.9	N/A	583	S6
	340 fs, 515 nm, 1 Hz	13.6	19.94	-480	-175	8.8	N/A	473	
Graphene/glass	35 fs, 800 nm, 1 kHz	74	2.06×10^4	-116×10^4	-2.8×10^6	136	N/A	450	S7
MoS_2/NMP	100 fs, 800 nm, 1 kHz	78.9	2.37	-46	-25.2	10.6	N/A	413	S8
MoS_2/NVP		84.7	1.66	-17.8	-10.3	6.2	N/A	833	
MoS_2/CHP		75.2	2.85	-58	-33	11.6	N/A	405	
$MoSe_2$/CHP	100fs, 800 nm, 1 kHz	45.3	7.93	-25.4	-14.5	1.8	N/A	590	S6
	340 fs, 515 nm, 1kHz	19.4	16.41	-3570	-900	54.8	N/A	43	
WS_2/glass	35 fs, 800 nm, 1 kHz	72	2.18×10^4	-76×10^4	-1.4×10^6	64.2	N/A	500	S7
BP/IPA	100 fs, 400 nm, 1 kHz	70.5	3.49	-162	-38.6	11.1	27.6	455.3	S9
	100 fs, 800 nm, 1 kHz	85.6	1.55	-61.7	-29.4	18.9	12.4	334.6	
BP/NMP	100 fs, 800 nm, 1 kHz	83.1	1.85	-40.8	-22.3	26.3	13.3	647.7	
$Ti_3C_2T_x$/glass	95 fs, 800 nm, 1 kHz	N/A	120	-117	-68.5	0.6	15-35	88.6	S10
	95 fs, 1064 nm, 1 kHz	N/A	120	-38.6	-29.6	0.25	10-40	61.2	

Table S4. NLO parameters (β: nonlinear absorption coefficient, γ′: nonlinear refractive index parameter, $Im\chi^{(3)}$: imaginary part of the third-order susceptibility, $Re\chi^{(3)}$: real part of the third-order susceptibility, and $\chi^{(3)}$: third-order susceptibility) of different concentration toluene dispersions of SiNS-tBuMA and SiNS-styrene determined by Z-scan, under 50 fs, 400 nm and 70 fs, 800 nm laser excitation.

λ (nm)	**Sample**	**c (mg/mL)**	**β (× 10^{-15} m/W)**	**γ' (× 10^{-21} m^2/W)**	**$Im\chi^{(3)}$ (× 10^{-16} esu)**	**$Re\chi^{(3)}$ (× 10^{-16} esu)**	**$\lvert\chi\rvert^{(3)}$ (× 10^{-16} esu)**
400	SiNS-tBuMA	0.07	-5.3 ± 0.8	4.0 ± 0.5	-1.55 ± 0.2	5.7 ± 0.7	5.9 ± 0.7
		0.10	-8.3 ± 0.8	6.0 ± 0.9	-2.5 ± 0.2	8.6 ± 1.0	9.0 ±1.0
		0.12	-10 ± 1.0	7.0 ± 1.0	-2.9 ± 0.3	10.0 ± 1.0	10.4 ± 1.0
	SiNS-styrene	0.05	-9.3 ± 1.0	8.4 ± 0.8	-2.7 ± 0.3	12.0 ± 1.0	12.3 ± 1.0
		0.10	-17 ± 2.0	15.7 ± 2.0	-5.0 ± 0.6	22.4 ± 3.0	23.0 ± 3.0
		0.14	-24 ± 3.0	22 ± 3.0	-7.0 ± 0.9	31.4 ± 4.0	32.2 ± 4.0
800	SiNS-tBuMA	0.10	165 ± 20	33.4 ± 5.0	94.1 ± 11.0	47.6 ± 7.0	105.4 ± 13.0
		0.14	220 ± 30	42 ± 7.0	125.5 ± 17.0	59.9 ± 10.0	139.1 ± 20.0
		0.20	335 ± 40	66 ± 5.0	191.1 ± 23.0	94.1 ± 7.0	213 ± 24.0
	SiNS-styrene	0.05	93 ± 2.0	28 ± 2.0	53.0 ± 1.0	39.9 ± 3.0	66.3 ± 3.0
		0.07	141 ± 6.0	58 ± 7.0	80.4 ± 3.0	82.7 ± 10.0	115.3 ± 10.0
		0.10	203 ± 9	74 ± 8.0	115.8 ± 5.0	105.5 ± 11.0	156.7 ± 12.0

Table S5. Third-order susceptibility values of different concentration toluene dispersions of SiNS-tBuMA and SiNS-styrene determined by OKE under 120 fs, 400 nm and 270 fs, 800 nm laser excitation.

λ (nm)	**Sample**	**c (mg/mL)**	**$\|\chi\|^{(3)}$ ($\times 10^{-16}$ esu)**
400	SiNS-tBuMA	0.05	3.8 ± 0.4
		0.07	5.0 ± 0.5
	SiNS-styrene	0.05	8.0 ± 1.0
		0.07	12 ± 1.0
800	SiNS-tBuMA	0.03	13 ± 1.0
		0.05	24 ± 2.0
	SiNS-styrene	0.03	29 ± 3.0
		0.05	38 ± 4.0

Table S6. NLO refraction-related parameters (γ': nonlinear refractive index parameter; $Re\chi^{(3)}$: real part of the third-order susceptibility; FOM: figure of merit (i.e., $Re\chi^{(3)}/\alpha_0$)) of SiNS-styrene, SiNS-tBuMA, MoX_2 (X=S, Se, Te), single-layered graphene (SLG), BP, and $Ti_3C_2T_x$.

Sample	**Excitation conditions**	**T (%)**	**α_0 (cm^{-1})**	**γ' ($\times 10^{-21}$ m^2/W)**	**$Re\chi^{(3)}$ ($\times 10^{-16}$ esu)**	**FOM ($\times 10^{-16}$ esu cm)**	**Ref.**
SiNS-styrene	50 fs, 400 nm, 10 Hz	79	2.55	15.7	22.4	8.8	this work
SiNS-tBuMA				6	8.6	3.4	
SiNS-styrene	70 fs, 800 nm, 10 Hz	90	1.0	74	105.5	105.5	
SiNS-tBuMA				33.4	47.6	47.6	
MoX_2/CHP	100 fs, 800 nm, 1 kHz	32.6-86.3	1.47-11.22	~0	~0	~0	S8
	340 fs, 515 nm, 1 kHz	7.94-87.6	1.32-25.34	~0	~0	~0	
SLG/ODCB	50 fs, 800 nm, 10 Hz		5.7	7.1	10.7	1.9	S11
BP/NMP	100 fs, 800 nm, 1 kHz	68	3.86	-(9.37-20.7)	-(13.6-30.1)	3.5-7.8	S12
$Ti_3C_2T_x$/glass	95 fs, 800 nm, 1 kHz	N/A	120	-46.6	-474	3.9	S10
	95 fs, 1064 nm, 1 kHz			-34.7	-353	2.9	

References

[S1] L. Ran, Z. Chai, Y. Gao, W. Wu, Q. Chang, D. Kong, *Curr. Appl. Phys.*, 2016, **16**, 985–988.

[S2] X. F. Jiang, L. Polavarapu, S. T. Neo, T. Venkatesan, Q. H. Xu, *J. Phys. Chem. Lett.*, 2012, **3**, 785–790.

[S3] G. Wang, D. Bennett, C. (John) Zhang, C. Ó Coileáin, M. Liang, N. McEvoy, J. J. Wang, J. Wang, K. Wang, V. Nicolosi, W. J. Blau, *Adv. Opt. Mater.*, 2020, **8**, 1902021.

[S4] M. Maldonado, M. L. da Silva Neto, P. G. Vianna, H. B. Ribeiro, V. O. Gordo, I. C. Carvalho, L. de S. Menezes, C. B. de Araújo, C. J. S. de Matos, L. Seixas, A. M. Jawaid, R. Busch, A. J. Ritter, R. A. Vaia, A. S. L. Gomes, *J. Phys. Chem. C*, 2020, **124**, 15425–15433.

[S5] C. Lu, M. Luo, Y. Ge, Y. Huang, Q. Zhao, Y. Zhou, X. Xu, *ACS Appl. Mater. Interfaces*, 2021, **14**, 2390–2400.

[S6] K. Wang, Y. Feng, C. Chang, J. Zhan, C. Wang, Q. Zhao, J. N. Coleman, L. Zhang, W. J. Blau, J. Wang, *Nanoscale*, 2014, **6**, 10530–10535.

[S7] C. Lu, C. Quan, K. Si, X. Xu, C. He, Q. Zhao, Y. Zhan, X. Xu, *Appl. Surf. Sci.*, 2019, **479**, 1161–1168.

[S8] K. Wang, J. Wang, J. Fan, M. Lotya, A. O'Neill, D. Fox, Y. Feng, X. Zhang, B. Jiang, Q. Zhao, H. Zhang, J. N. Coleman, L. Zhang, W. J. Blau, *ACS Nano*, 2013, **7**, 9260–9267.

[S9] S. B. Lu, L. L. Miao, Z. N. Guo, X. Qi, C. J. Zhao, H. Zhang, S. C. Wen, D. Y. Tang, D. Y. Fan, *Opt. Express*, 2015, **23**, 11183–11194.

[S10] X. Jiang, S. Liu, W. Liang, S. Luo, Z. He, Y. Ge, H. Wang, R. Cao, F. Zhang, Q. Wen, J. Li, Q. Bao, D. Fan, H. Zhang, *Laser Photonics Rev.*, 2017, **12**, 1700229.

[S11] M. Stavrou, I. Dalamaras, N. Karampitsos, S. Couris, *J. Phys. Chem. C*, 2020, **124**, 27241–27249.

[S12] Y. Xu, F. Jiang, Y. Ge, Z. Guo, Z. Zeng, Q.-H. Xu, H. Zhang, X.-F. Yu, D. Fan, *J. Mater. Chem. C*, 2017, **5**, 3007–3013.