Supporting Information

Systematic Study of the Structure-Property Relationship of a series of Nonlinear Optical Julolidinyl-based Chromophores with Thieno[3,2-b]thiophene moiety

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1. Electrochemical figures.

2. Quantum chemical calculations.

1. Electrochemical figures.

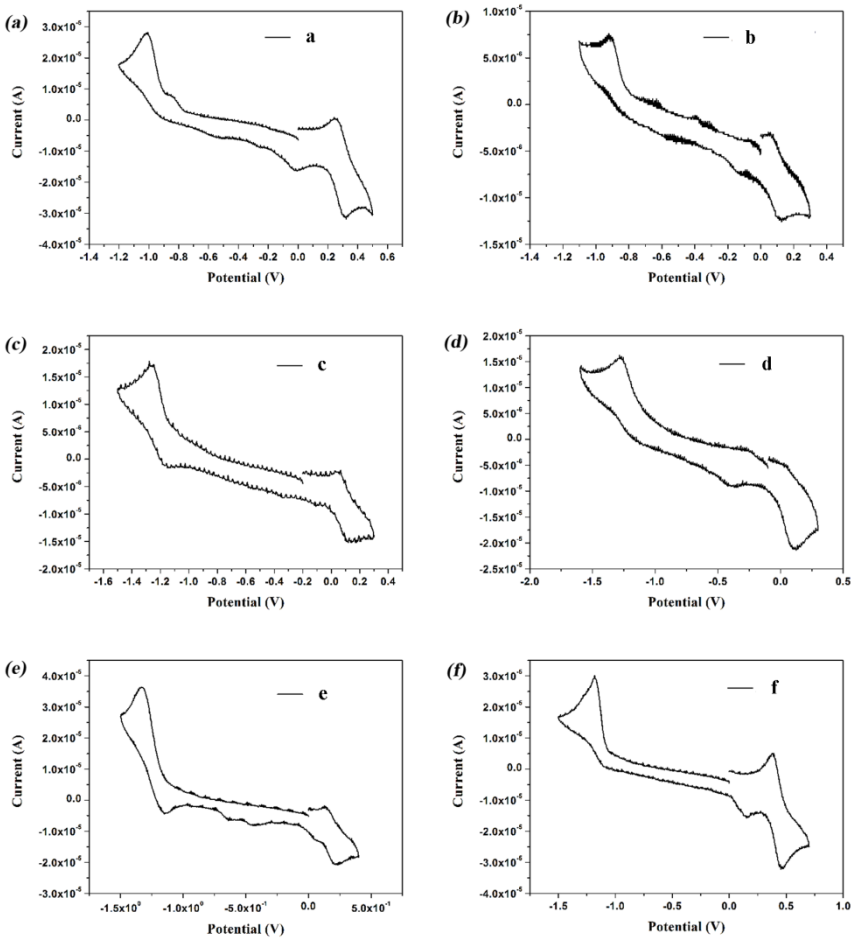

Fig. S1 Cyclic voltammogram of chromophores a-f recorded in acetronitrile with a scan rate of 50 mV/s using tetrabutylammonium hexafluorophosphate supporting electrolyte.

2. Quantum chemical calculations.

DFT calculations were performed using Gaussian 09 employing the hybrid B3LYP exchange-correlation functional with asplit valence 6-31G basis set.

Table S1. Calculated polarizability (α) of chromophores a-f in gas phase and six different solvents (in 10^2a.u.).

Sol	a	b	c	d	e	f
VC	7.13	9.76	6.52	9.26	5.19	5.13
DO	8.63	12.5	8.11	1.15	6.19	6.11
TL	8.76	12.8	8.25	11.7	6.28	6.19
CF	9.81	14.8	9.40	13.3	6.99	6.86
DC	10.5	16.3	10.2	14.3	7.47	7.30
AC	11.0	17.4	10.8	15.1	7.84	7.63
AN	11.2	17.8	11.0	15.4	7.97	7.75

[a]: VC: vacuum; DO: 1,4-dixoane; TL: toluene; CF: chloroform; DC: dichloromethane; AC: acetone; AN: acetonitrile.

Table S2. Calculated hyperpolarizability (β_x and β_{tot}) of chromophores a-f in gas phase and six different solvents (in 10^{-30}esu).

	a		b		c		d		e		f	
Sol	β_x	β_{tot}[a]	β_x	β_{tot}[a]	β_x	β_{tot}[a]	β_x	β_{tot}[a]	β_x	β_{tot}[a]	β_x	β_{tot}[a]
VC	320.45	322.98	1684.18	1684.69	677.19	678.91	1685.89	1686.59	240.34	245.12	143.99	150.35
DO	575.20	582.50	3471.07	3472.29	1404.17	1407.07	3484.74	3487.17	448.54	456.08	256.06	268.06
TL	597.22	605.15	3649.43	3650.74	1478.55	1481.55	3668.31	3670.94	468.65	476.49	265.85	278.40
CF	768.54	782.44	5303.40	5305.68	2183.95	2188.15	5388.99	5393.73	650.66	661.20	341.49	359.70
DC	859.90	879.66	6536.14	6539.32	2732.71	2737.88	6712.57	6719.14	782.63	795.35	384.22	407.05
AC	915.40	940.50	7553.62	7557.70	3203.75	3209.83	7839.77	7847.98	890.27	904.88	410.35	437.40
AN	929.98	957.40	7943.83	7948.27	3388.49	3394.88	8272.02	8280.96	930.86	946.31	418.19	446.97

a $\beta_{tot} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$, [a]: VC: vacuum; DO: 1,4-dixoane; TL: toluene; CF: chloroform; DC: dichloromethane; AC: acetone; AN: acetonitrile.

Table S3. Calculated dipole moments (μ_x and μ_{tot}) of chromophores a-f in gas phase and six different solvents (in D).

	a		b		c		d		e		f	
	μ_x	μ_{tot}[a]	μ_x	μ_{tot}[a]	μ_x	μ_{tot}[a]	μ_x	μ_{tot}[a]	μ_x	μ_{tot}[a]	μ_x	μ_{tot}[a]
VC	22.22	22.43	24.62	25.76	16.80	17.91	16.14	17.62	13.54	14.12	19.48	21.42
DO	27.30	27.52	30.17	31.50	20.21	20.51	19.15	20.88	16.51	17.41	23.69	24.28
TL	27.71	27.93	30.63	31.79	20.47	20.78	19.38	21.13	16.74	17.66	24.03	24.63
CF	31.03	31.27	34.21	35.68	22.55	22.89	21.15	23.06	18.58	19.60	26.76	27.43
DC	33.16	33.41	36.52	38.06	23.84	24.18	22.18	24.18	19.75	20.82	28.47	29.20
AC	34.72	35.00	38.25	39.84	24.76	25.13	22.94	25.01	20.62	21.73	29.76	30.53
AN	35.30	35.59	38.89	40.49	25.10	25.47	23.18	25.29	20.95	22.07	30.22	31.01

a $\mu_{tot} = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$, [a]: VC: vacuum; DO: 1,4-dixoane; TL: toluene; CF: chloroform; DC: dichloromethane; AC: acetone; AN: acetonitrile.

Table S4. Calculated $\mu\beta_{tot}$ of chromophores a-f in gas phase and six different solvents (in 10^{-48}esu).

Sol	a	b	c	d	e	f
VC	7243.42	43401.78	12158.12	29723.92	3461.67	3220.80
DO	16031.54	109388.97	28862.58	72811.44	7943.61	6508.60
TL	16901.90	116067.36	30786.44	77565.56	8415.60	6856.99
CF	24468.29	189311.89	50075.83	124353.71	12961.14	9867.11
DC	29391.55	248874.81	66215.36	162487.57	16562.47	11884.10
AC	32917.00	301099.66	80647.12	196307.80	19664.58	13353.79
AN	34070.61	321849.30	86471.37	209411.37	20881.67	13861.82

[a]:$\mu\beta_{tot} = \mu_{tot} \times \beta_{tot}$, [b]: VC: vacuum; DO: 1,4-dixoane; TL: toluene; CF: chloroform; DC: dichloromethane; AC: acetone; AN: acetonitrile.

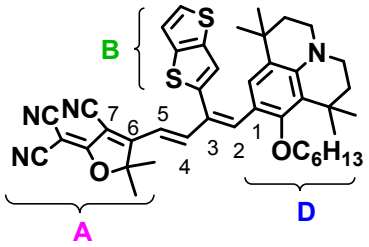

Fig. S2 Numbering of the carbon atoms in the conjugated bridge for chromophore a

Table S5. Bond lengths of the conjugated chain of chromophore **a** obtained by full geometry optimizations using 6-31G basis set as a function of solvent (in Å) (Atom numbering in Fig. S1).

Sol	C_1-C_2	C_2-C_3	C_3-C_4	C_4-C_5	C_5-C_6	C_6-C_7	BLA
VC	1.438	1.387	1.443	1.374	1.423	1.392	-0.050
DO	1.432	1.392	1.437	1.379	1.417	1.398	-0.039
TL	1.431	1.393	1.437	1.379	1.417	1.399	-0.038
CF	1.428	1.396	1.432	1.383	1.412	1.403	-0.030
DC	1.425	1.398	1.430	1.385	1.409	1.406	-0.025
AC	1.423	1.400	1.427	1.387	1.407	1.408	-0.021
AN	1.422	1.401	1.427	1.388	1.406	1.409	-0.019

[a]: VC: vacuum; DO: 1,4-dixoane; TL: toluene; CF: chloroform; DC: dichloromethane; AC: acetone; AN: acetonitrile.

Table S5'. Mulliken atomic charges on various molecular domains for chromophore **a** at the

B3LYP/6-31G level. The moieties in color were considered for charge calculation.

	VC	DO	TL	CF	DC	AC	AN
D	0.2033	0.2282	0.2340	0.2428	0.2770	0.2540	0.2898
B	0.0372	0.0384	0.0389	0.0388	0.0388	0.0392	0.0379
A	-0.3299	-0.3806	-0.3901	-0.4113	-0.4425	-0.4366	-0.4604

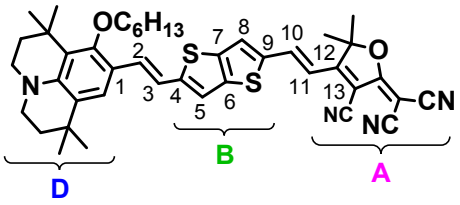

Fig. S3 Numbering of the carbon atoms in the conjugated bridge for chromophore **b**

Table S6. Bond lengths of the conjugated chain of chromophore **b** obtained by full geometry optimizations using 6-31G basis set as a function of solvent (in Å) (Atom numbering in Fig. S2).

Sol	C_1-C_2	C_2-C_3	C_3-C_4	C_4-C_5	C_5-C_6	C_6-C_7	C_7-C_8	C_8-C_9	C_9-C_{10}	C_{10}-C_{11}	C_{11}-C_{12}	C_{12}-C_{13}	BLA
VC	1.448	1.367	1.428	1.391	1.408	1.399	1.402	1.395	1.417	1.376	1.421	1.393	-0.034
DO	1.444	1.370	1.425	1.393	1.405	1.402	1.399	1.399	1.412	1.380	1.415	1.398	-0.026
TL	1.444	1.370	1.425	1.394	1.405	1.403	1.398	1.399	1.412	1.381	1.415	1.399	-0.026
CF	1.442	1.372	1.423	1.396	1.403	1.405	1.396	1.401	1.408	1.384	1.411	1.402	-0.020
DC	1.440	1.373	1.422	1.397	1.402	1.406	1.394	1.403	1.406	1.386	1.408	1.405	-0.018
AC	1.439	1.374	1.421	1.398	1.401	1.407	1.393	1.404	1.404	1.388	1.407	1.407	-0.015
AN	1.439	1.375	1.420	1.398	1.400	1.407	1.393	1.404	1.404	1.388	1.406	1.408	-0.014

[a]: VC: vacuum; DO: 1,4-dixoane; TL: toluene; CF: chloroform; DC: dichloromethane; AC: acetone; AN: acetonitrile.

Table S6'. Mulliken atomic charges on various molecular domains for chromophore **b** at the B3LYP/6-31G level. The moieties in color were considered for charge calculation.

	VC	DO	TL	CF	DC	AC	AN
D	0.2189	0.2569	0.2439	0.2868	0.3037	0.2671	0.3212
B	-0.0243	-0.0137	-0.0164	-0.0053	0.0063	-0.0085	0.0069
A	-0.2616	-0.3243	-0.3166	-0.3710	-0.3875	-0.3715	-0.4248

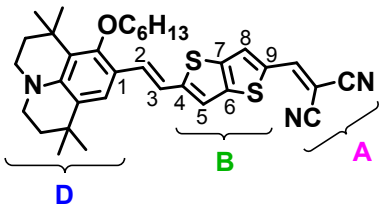

Fig. S4 Numbering of the carbon atoms in the conjugated bridge for chromophores **c**

Table S7. Bond lengths of the conjugated chain of chromophore **c** obtained by full geometry optimizations using 6-31G basis set as a function of solvent (in Å) (Atom numbering in Fig. S3).

Sol	C_1-C_2	C_2-C_3	C_3-C_4	C_4-C_5	C_5-C_6	C_6-C_7	C_7-C_8	C_8-C_9	BLA
VC	1.449	1.366	1.430	1.389	1.410	1.399	1.400	1.398	-0.034
DO	1.446	1.368	1.427	1.392	1.407	1.401	1.397	1.400	-0.029
TL	1.446	1.369	1.427	1.392	1.407	1.401	1.397	1.400	-0.029
CF	1.444	1.370	1.425	1.394	1.406	1.403	1.395	1.402	-0.025
DC	1.442	1.371	1.424	1.394	1.404	1.403	1.394	1.403	-0.023
AC	1.442	1.372	1.424	1.395	1.404	1.404	1.394	1.404	-0.022
AN	1.441	1.372	1.423	1.396	1.404	1.404	1.393	1.404	-0.021

[a]: VC: vacuum; DO: 1,4-dixoane; TL: toluene; CF: chloroform; DC: dichloromethane; AC: acetone; AN: acetonitrile.

Table S7'. Mulliken atomic charges on various molecular domains for chromophore **c** at the B3LYP/6-31G level. The moieties in color were considered for charge calculation.

	VC	DO	TL	CF	DC	AC	AN
D	0.2033	0.2282	0.2340	0.2428	0.2770	0.2540	0.2898
B	0.0372	0.0384	0.0389	0.0388	0.0388	0.0392	0.0379
A	-0.3299	-0.3806	-0.3901	-0.4113	-0.4425	-0.4366	-0.4604

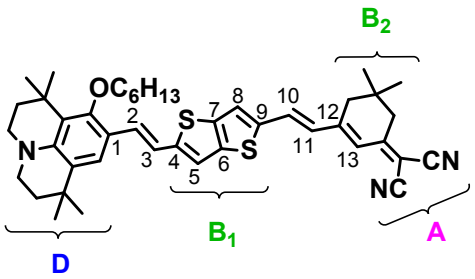

Fig. S5 Numbering of the carbon atoms in the conjugated bridge for chromophores **d**

Table S8. Bond lengths of the conjugated chain of chromophores **d** obtained by full geometry optimizations using 6-31G basis set as a function of solvent (in Å) (Atom numbering in Fig. S4).

Sol	C_1-C_2	C_2-C_3	C_3-C_4	C_4-C_5	C_5-C_6	C_6-C_7	C_7-C_8	C_8-C_9	C_9-C_{10}	C_{10}-C_{11}	C_{11}-C_{12}	C_{12}-C_{13}	BLA
VC	1.452	1.364	1.432	1.387	1.412	1.394	1.408	1.390	1.425	1.369	1.439	1.379	-0.047
DO	1.450	1.366	1.431	1.388	1.411	1.395	1.407	1.391	1.423	1.371	1.437	1.382	-0.044
TL	1.450	1.366	1.430	1.389	1.411	1.395	1.407	1.391	1.423	1.371	1.437	1.382	-0.044
CF	1.449	1.367	1.430	1.389	1.410	1.396	1.406	1.392	1.422	1.372	1.436	1.384	-0.042
DC	1.448	1.368	1.429	1.390	1.410	1.396	1.406	1.392	1.421	1.372	1.435	1.385	-0.041
AC	1.448	1.368	1.429	1.390	1.410	1.397	1.406	1.392	1.421	1.373	1.434	1.386	-0.040
AN	1.448	1.368	1.429	1.390	1.410	1.397	1.406	1.392	1.420	1.373	1.434	1.385	-0.040

[a]: VC: vacuum; DO: 1,4-dixoane; TL: toluene; CF: chloroform; DC: dichloromethane; AC: acetone; AN: acetonitrile.

Table S8'. Mulliken atomic charges on various molecular domains for chromophore **d** at the B3LYP/6-31G level. The moieties in color were considered for charge calculation.

	VC	DO	TL	CF	DC	AC	AN
D	0.1773	0.1972	0.2001	0.2113	0.2027	0.2051	0.2257
B_1	-0.0717	-0.0774	-0.0781	-0.0812	-0.0840	-0.0855	-0.0840
B_2	0.3171	0.3437	0.3458	0.3602	0.3709	0.3773	0.3761
A	-0.4147	-0.4695	-0.4739	-0.5027	-0.5101	-0.5202	-0.5372

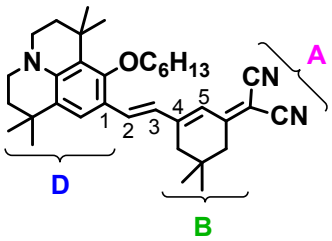

Fig. S6 Numbering of the carbon atoms in the conjugated bridge for chromophores e

Table S9. Bond lengths of the conjugated chain of chromophore **e** obtained by full geometry optimizations using 6-31G basis set as a function of solvent (in Å) (Atom numbering in Fig. S5).

Sol	C_1-C_2	C_2-C_3	C_3-C_4	C_4-C_5	BLA
VC	1.449	1.368	1.441	1.380	-0.071
DO	1.446	1.371	1.439	1.384	-0.065
TL	1.446	1.371	1.438	1.384	-0.064
CF	1.444	1.373	1.436	1.387	-0.060
DC	1.442	1.374	1.435	1.388	-0.057
AC	1.441	1.375	1.434	1.389	-0.055
AN	1.441	1.376	1.433	1.390	-0.054

[a]: VC: vacuum; DO: 1,4-dixoane; TL: toluene; CF: chloroform; DC: dichloromethane; AC: acetone; AN: acetonitrile.

Table S9'. Mulliken atomic charges on various molecular domains for chromophore **d** at the B3LYP/6-31G level. The moieties in color were considered for charge calculation.

	VC	DO	TL	CF	DC	AC	AN
D	0.2083	0.2315	0.2332	0.2457	0.2528	0.2578	0.2595
B	0.2977	0.3212	0.3229	0.3359	0.3436	0.3490	0.3510
A	-0.4378	-0.4877	-0.4914	-0.5191	-0.5351	-0.5464	-0.5504

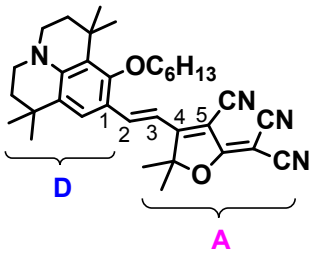

Fig. S7 Numbering of the carbon atoms in the conjugated bridge for chromophores **f**

Table S10. Bond lengths of the conjugated chain of chromophore **f** obtained by full geometry optimizations using 6-31G basis set as a function of solvent (in Å) (Atom numbering in Fig. S6).

Sol	C_1-C_2	C_2-C_3	C_3-C_4	C_4-C_5	BLA
VC	1.440	1.376	1.424	1.394	-0.047
DO	1.434	1.381	1.418	1.399	-0.036
TL	1.433	1.381	1.417	1.400	-0.035
CF	1.430	1.384	1.413	1.404	-0.027
DC	1.427	1.386	1.410	1.407	-0.022
AC	1.425	1.388	1.408	1.409	-0.018
AN	1.425	1.389	1.407	1.410	-0.017

[a]: VC: vacuum; DO: 1,4-dixoane; TL: toluene; CF: chloroform; DC: dichloromethane; AC: acetone; AN: acetonitrile.

Table S10'. Mulliken atomic charges on various molecular domains for chromophore **f** at the B3LYP/6-31G level. The moieties in color were considered for charge calculation.

	VC	DO	TL	CF	DC	AC	AN
D	0.2531	0.3301	0.3364	0.3558	0.3690	0.3783	0.3816
A	-0.2933	-0.3419	-0.3455	-0.3734	-0.3899	-0.4017	-0.4059