Supporting Information

Methyl Made Noncentrosymmetric Stacking: A Promising Organic Single Crystal for Highly Efficient Terahertz-wave Generation

Jingkai Shi, Yixin He, Fei Liang, Xinyuan Zhang,* Degang Xu, Jiyong Yao, Guochun Zhang, Zhanggui Hu, Jianquan Yao, and Yicheng Wu

[a]*Tianjin Key Laboratory of Functional Crystal Materials, Institute of Functional Crystals, Tianjin University of Technology, Tianjin 300384, China.*

Email: xyzhang@email.tjut.edu.cn

[b]*The Institute of Laser & Optoelectronics, College of Precision Instruments and Opto-electronics Engineering, Tianjin University, Tianjin 300072, China.*

[c]*Key Laboratory of Optoelectronic Information Technology (Ministry of Education), Tianjin University, Tianjin 300072, China.*

[d]*State Key Laboratory of Crystal Materials and Institute of Crystal Materials, Shandong University, Jinan 250100, China.*

[e]*Key Laboratory of Functional Crystals and Laser Technology, Beijing Center for Crystal Research and Development, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China.*

1. Supplementary figures.

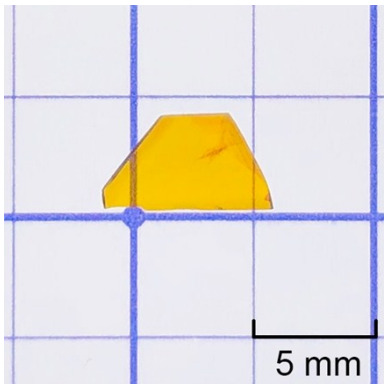


Figure S1. OHI-T single crystal grown from methanol solvent.

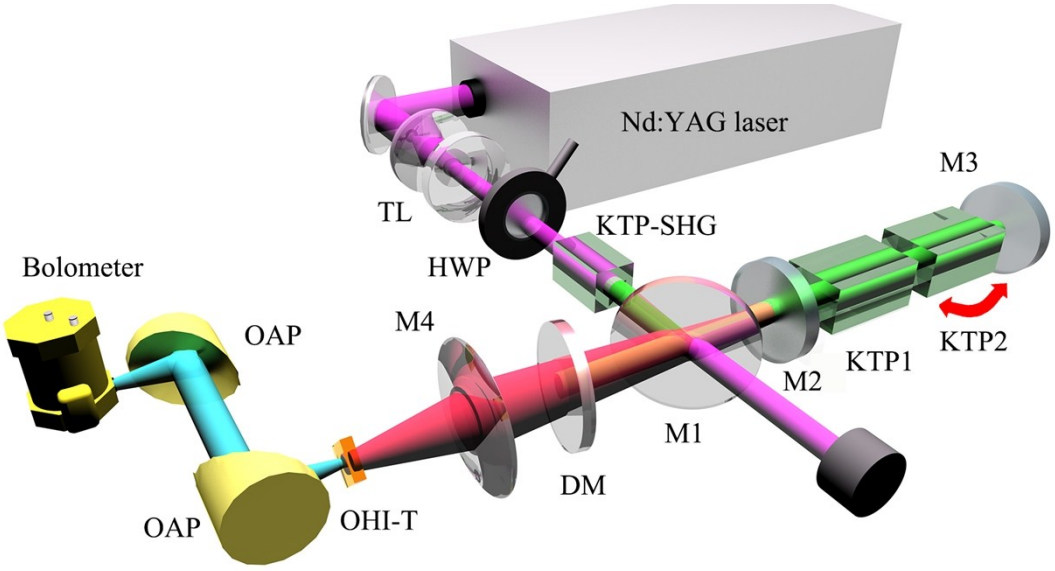


Figure S2. Schematic diagram of the experimental setup for THz wave output.

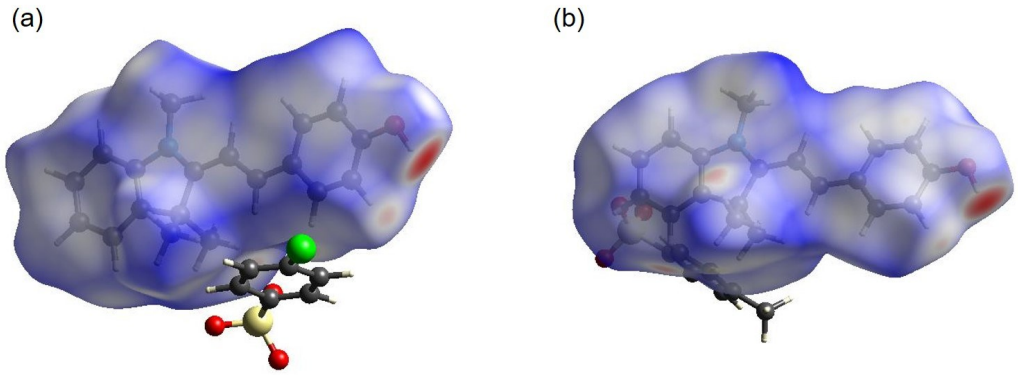


Figure S3. Hirsfield surfaces of (a) OHI-CBS and (b) OHI-T.

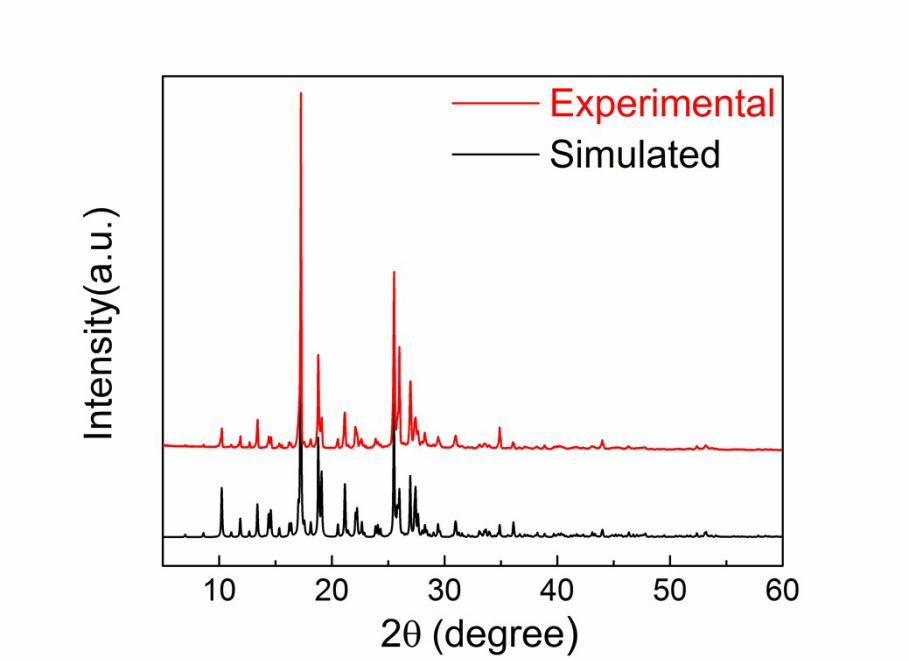


Figure S4. Simulated (black), experimental (red) PXRD patterns of OHI-CBS.

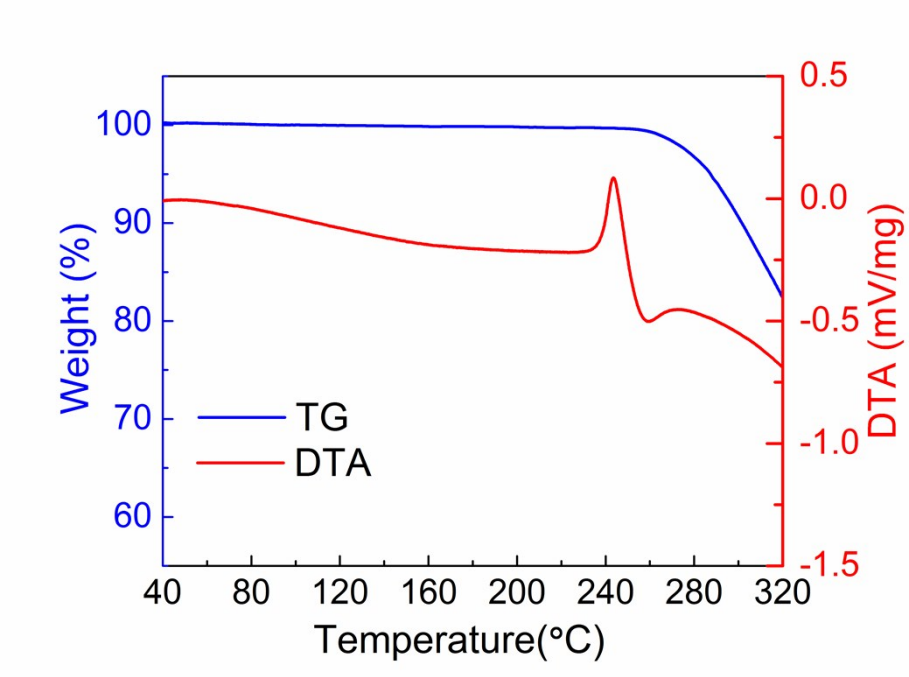


Figure S5. TG and DTA curves of OHI-CBS crystals.

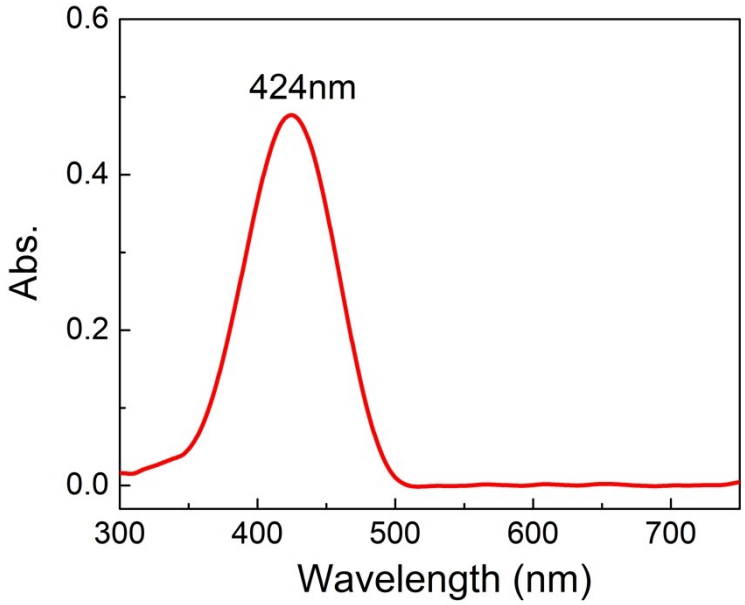
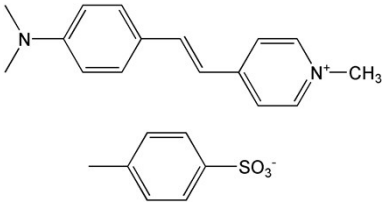
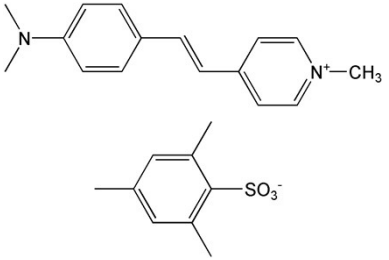
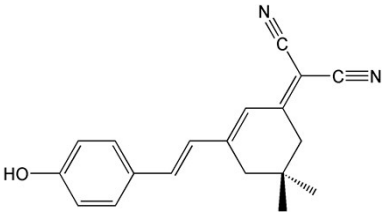
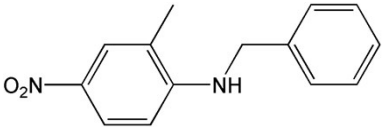
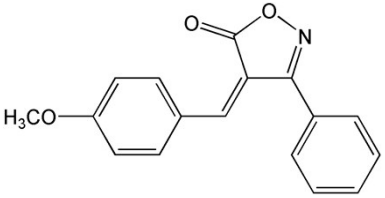
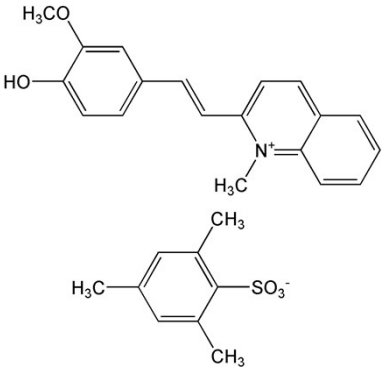
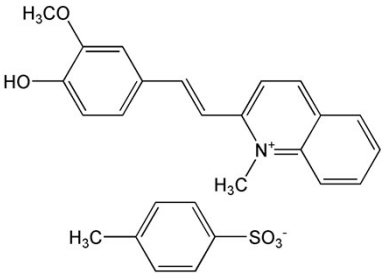


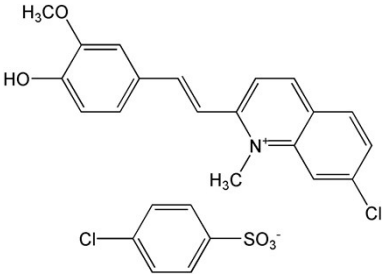
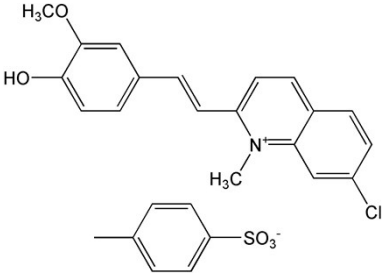
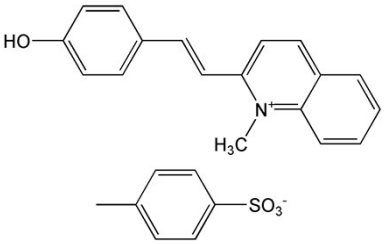
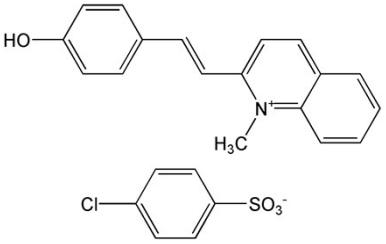
Figure S6. UV-vis spectra of OHI-T in acetonitrile.

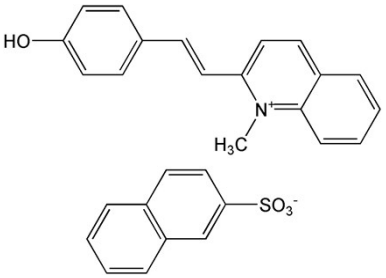
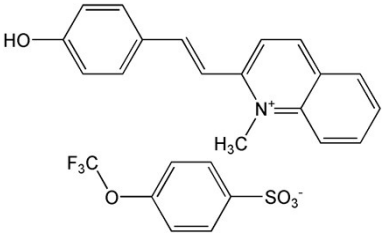
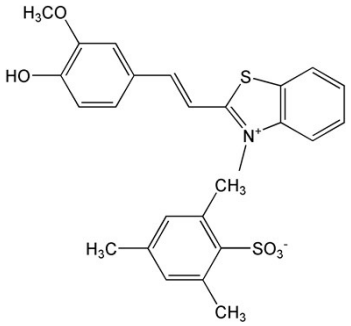
2. Supplementary tables.

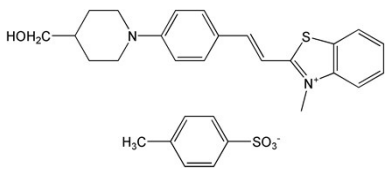
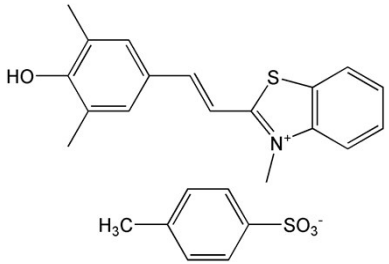
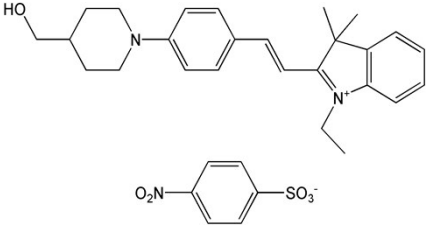
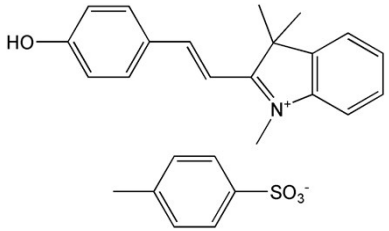
Table S1. Comparison of mentioned organic NLO crystals.

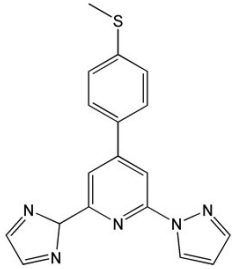
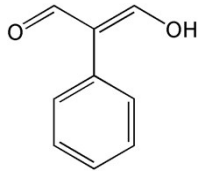
Series	Crystal Name	Chemical Structure	Space Group	NLO Coefficients/ SHG Intensity	Cut-off Wavelengths	THz-wave Generation	Ref.
Pyridinium-based	DAST		*C*c	d_{11} = 210 pm/V at 1.9 μm	680 nm	DFG: 0.3-19.6 THz	8, 9, 46
	DSTMS		*C*c	d_{11} = 214 pm/V at 1.9 μm	-	DFG: 0.88-19.27 THz	9, 47
Isophorone-based	OH1		$Pna2_1$	d_{33} = 120 pm/V at 1.9 μm	640 nm	DFG: 0.02 - 20 THz	10, 11, 45

Nitraniline-based	BNA		$P\mathrm{na2_1}$	d_{33} = 234 pm/V at 1064 nm	-	DFG: 0.1-15 THz	12
Isoxazolone-based	MLS		$P\mathrm{na2_1}$	1.5×OH1 at 2.09 μm	470 nm	DFG: 1.23-14.09 THz, 16.90-18.59 THz	20, 21
Quinolinium-based	HMQ-TMS		$P\mathrm{n}$	-	595 nm	OR: ~ 6 THz	15
	HMQ-T		$P\mathrm{n}$	0.6×DAST at 1.9 μm	595 nm	OR: ~ 2 THz	14

HM7ClQ-CBS		*P*na2$_1$	Comparable to HMQ-T at 1400 nm	-	OR: ~ 8 THz	16
HM7ClQ-T		*P*na2$_1$	Comparable to HMQ-T at 1400 nm	-	OR: ~ 8 THz	16
OHQ-T		*P*n	Comparable to DAST at 1253 nm	510 nm	OR: ~ 10 THz	17
OHQ-CBS		*P*1	-	550 nm	OR: ~ 9 THz	18

	OHQ-N2S		*P*n	Comparable to DAST at 1253 nm	490 nm	OR: ~ 6 THz	19
	OHQ-TFO		*P*c	2.3×OHQ-T at 1140 nm	610 nm	OR: ~ 8 THz	13
Benzothiazolium-based	HMB-TMS		*P*n	Comparable to DAST at 1250 nm	580 nm	OR: ~ 5.3 THz	22

	PMB-T		*C*c	Comparable to DAST at 1800 nm	680 nm	OR: ~ 8.0 THz	23
	HDB-T		$P2_1$	1.5×OH1 at 2.09 μm	-	DFG: 0.1-20 THz	24
Indolium-based	EHPSI-4NBS		*P*n	-	-	OR: ~3.8 THz	32
	OHI-T		*C*c	0.7× OH1 at 2.09 μm	504 nm	DFG: 0.1- 20 THz	This work

UOH1		$I4_1$	3.3× urea at 800 nm	-	OR: ~ 2.2 THz	25
PhMDA		$Pna2_1$	-	-	OR: ~ 2 THz	26