Design, Crystal Structures and Enhanced Frequency -upconverted Lasing Efficiency of a New Series of Dyes from Hybrid of Inorganic Polymers and Organic Chromophores

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General methods

All chemicals were obtained from commercial sources and used as received. All the solvents used for measurement were purified by the standard methods. IR spectra were recorded with a Nicolet FT-IR Nexus 870 instrument (KBr discs) in the 400-4000cm^{-1} region. ^{1}HNMR spectra were performed on Bruker 400 MHz Ultrashield spectrometer and are reported as parts per million (ppm) from TMS (δ). Elemental analysis was performed with a Perkin-Elmer 240 instrument. Thermogravimetric Analysis analyses were recorded with a Perkin-Elmer Pris-1 DMDA-V1 analyzer in an atmosphere of nitrogen at a heating rate of 5 °C min^{-1}. Electrospray ionisation mass spectra (ESI-MS) were obtained from Finnigan LCQ Spectrometer. The UV-visible-near-IR spectra were measured on Hitachi U-3500 UV-vis-IR recording spectrophotometer by using quartz cuvettes of 1 cm path length. One-photon fluorescence spectra were measured on a Perkin Elmer LS-55B fluorospectrometer.

Two-photon excited fluorescence (1×10^{-2} M) was measured using the 1064 nm, 40 ps pulse laser. The TPP lasing experiments: the 1064 nm, 40 ps pulse from a passively mode-locked Nd:YAG laser was adopted as pump source. Though a f = 12 cm lens, the pump beam was focused vertically onto the center of a 1 cm path quartz cell that was full of solution sample. The lasing output beam was dispersed by a polychromator and the spectra were recorded by a streak camera (Hamamatsu Model C1587).

The TPA cross-section values of the dyes were measured using two-photon induced fluorescence method. The excitation source for the TPIF (two-photon induced fluorescent) experiments was a mode-locked femtosecond Ti:Sapphire laser (Spectra-physics, 100 fs, 82 Hz). The maximum average laser power available for these was about 300 mW. An optical multi-channel analyzer was used as a recorder. The experimental set-up for the TPIF excitation cross-section measurements was similar to that used by Xu (C. Xu and W. W. Web, *J. Opt. Soc. Am. B*, **1996**, *13*, 481; M. A. Albota, C. Xu and W. W. Webb, *Appl. Opt.*, **1998**, *13*, 481). In brief, the femtosecond laser was split into two beams. The weaker one was used as a reference beam and monitored by the detector of a power meter (Coherent, FieldMaster NO.33-0506). The intense beam was focused on the sample by a lens. Using a telescopic system the up-converted fluorescence was firstly collected at a direction perpendicular to the pumped beam, and then passed through a liquid barrier filter (1 cm pathlength, 1 mol l^{-1} $CuSO_4$ solution) to exclude excitation illumination. To minimize the re-absorption effect, the excitation beam was focused as closely as possible on the front wall of the quartz cell. A photomultiplier tube (Hamamatsu R928) was used for the TPIF detector and the signal was read using lock-in Amplifier (EG&G 5210).

X-ray crystallographic studies

Crystal data for all dyes

Table S1 Crystallographic data

Compound	4′	3′	1	2	3	4
Empirical formula	$C_{22}H_{35}IN_2O_2$	$C_{20}H_{29}IN_2O$	$C_{19}H_{19}CdN_5S_3$	$C_{23}H_{26}CdN_6S_3$	$C_{23}H_{27}CdN_5S_3$	$C_{25}H_{31}CdN_5S_3$
Formula weight	486.42	440.35	525.97	595.08	582..08	610.13
Crystal system	Triclinic	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic	Momoclinic
Space group	P-1	$P2_1/c$	Pbca	$P2_1/n$	Pbca	$P2_1/n$
a [Å]	8.5069(10)	15.0256(12)	14.3163(3)	12.906(2)	14.287(3)	12.7935(16)
b [Å]	9.9764(14)	8.8242(10)	10.7538(3)	10.8887(16)	10.751(2)	10.7453(15)
c [Å]	15.945(2)	17.4227(18)	28.2371(7)	19.289(4)	34.037(7)	20.771(3)
α [°]	87.271(9)	90	90	90	90	90
β [°]	79.544(9)	115.336(6)	90	95.610(14)	90	99.639(11)
γ [°]	65.359(10)	90	90	90	90	90
V [Å^3]	1209.0(3)	2087.9(4)	4347.23(19)	2697.7(8)	5228.2(18)	2815.1(7)
Z	2	4	8	4	8	4
D_{calcd} [g/cm^3]	1.336	1.401	1.607	1.465	1.479	1.440
$F(000)$	500	896	2112	1208	2368	1248
$\theta_{min-max}$ [°]	2.25, 25.00°	2.37, 24.98°	1.44, 28.30	1.82, 25.00	1.20, 28.48	1.99, 25.00
N_{ref}	5191	4723	29135	6010	32634	6327
N_{uni}, N_{par}	4250, 260	3689, 217	5361, 254	4734, 301	6562, 292	4956, 307
R_1	0.0412,	0.0354,	0.0466,	0.0396,	0.0413	0.0387,
wR_2	0.0966	0.0765	0.0992	0.1015	0.1036	0.0785
Gof	1.015	0.988	0.937	1.034	1.090	0.998

Table S2 Selected bond lengths (Å) for 3′ and 4′

3′		4′	
N(1)-C(1)	1.477	N(1)-C(1)	1.477
N(2)-C(12)	1.364	N(2)-C(12)	1.365
C(4)-C(7)	1.465	C(4)-C(7)	1.443
C(7)-C(8)	1.315	C(7)-C(8)	1.340
C(8)-C(9)	1.459	C(8)-C(9)	1.464

Table S3 Selected bond lengths (Å) and angles (º) for **4**

Cd(1)-N(5)	2.330	S(2)-C(24)	1.646	N(4)-Cd(1)-S(2)	172.56	C(24) -N(4)-Cd(1)	148.34
Cd(1)-N(3)	2.267	N(5)-C(25)	1.158	N(4)-Cd(1)-N(5)	84.69	C(23) -N(3)-Cd(1)	157.11
Cd(1)-N(4)	2.371	N(4)-C(24)	1.139	N(3)-Cd(1)-S(3)	91.11	N(4) -C(24)-S(2)	178.38
Cd(1)-S(1)	2.707	N(3)-C(23)	1.144	S(2)-Cd(1)-S(3)	93.75	N(5) -C(25)-S(3)	178.56
Cd(1)-S(2)	2.735	N(5)-Cd(1)-S(1)	90.39	C(25)-S(3)-Cd(1)	101.39	N(3) -C(23)-S(1)	179.52
Cd(1)-S(3)	2.746	N(4)-Cd(1)-S(1)	90.00	C(23)-S(1)-Cd(1)	95.06		
S(1)-C(23)	1.648	N(3)-Cd(1)-S(1)	172.36	C(24)-S(2)-Cd(1)	98.16	C(25) -N(5)-Cd(1)	138.63
S(3)-C(25)	1.645	N(5)-Cd(1)-S(3)	171.52	C(25) -N(5)-Cd(1)	138.63	N(3)-Cd(1)-S(2)	91.13

Table S4 Selected bond lengths (Å) and angles (º) for dye 1, 2 and 3

1		2		3	
Cd(1)-N(3)	2.283	Cd(1)-N(5)	2.368	Cd(1)-N(4)	2.362
Cd(1)-N(5)#1	2.349	Cd(1)-N(4)	2.338	Cd(1)-N(3)	2.319
Cd(1)-N(4)#1	2.358	Cd(1)-N(3)	2.289	Cd(1)-N(5)	2.276
Cd(1)-S(1)#1	2.7060	Cd(1)-S(3)	2.718	Cd(1)-S(1)	2.707
Cd(1)-S(2)	2.7398	Cd(1)-S(2)	2.737	Cd(1)-S(2)	2.775
Cd(1)-S(3)	2.7656	Cd(1)-S(1)	2.741	Cd(1)-S(3)	2.715
S(1)-C(17)	1.631	S(1)-C(19)	1.654	S(1)-C(21)	1.642
S(2)-C(18)	1.662	S(2)-C(20)	1.649	S(2)-C(22)	1.637
S(3)-C(19)	1.653	S(3)-C(21)	1.641	S(3)-C(23)	1.643
N(3)-C(17)	1.157	C(20)-N(4)	1.153	N(5)-C(23)	1.151
N(4)-C(19)	1.135	C(19)-N(3)	1.146	N(4)-C(22)	1.154
N(5)-C(18)	1.136	C(21)-N(5)	1.152	N(3)-C(21)	1.154
N(5) -Cd(1)- N(4)	83.87	S(3)-Cd(1)-S(2)	92.30	N(4)-Cd(1)-S(1)	174.05
N(3)-Cd(1)-S(1)	176.05	N(3)-Cd(1)-S(1)	171.66	N(5)-Cd(1)-S(3)	175.12
N(5) -Cd(1)- S(1)	91.73	N(5)-Cd(1)-N(4)	83.43	N(3)-Cd(1)-S(2)	169.64
N(4) -Cd(1)- S(1)	89.98	N(3)-Cd(1)-S(3)	92.13	N(5)-Cd(1)-S(2)	90.82
N(3)-Cd(1)-S(2)	93.09	N(3)-Cd(1)-S(2)	89.59	N(5)-Cd(1)-S(1)	93.06
N(4) -Cd(1)-S(2)	174.24	N(5)-Cd(1)-S(3)	175.06	N(3)-Cd(1)-S(3)	92.70
N(3)-Cd(1)-S(3)	91.05	N(4)-Cd(1)-S(2)	171.53	N(4)-Cd(1)-S(3)	90.05
N(5) -Cd(1)-S(3)	171.61	N(5)-Cd(1)-S(1)	88.66	S(2)-Cd(1)-S(1)	94.24
S(2)-Cd(1)-S(3)	93.48	N(4)-Cd(1)-S(1)	90.91	N(3)-Cd(1)-N(4)	83.01
C(17)-S(1)-Cd(1)	95.56	C(19)-S(1)-Cd(1)	95.82	C(23)-S(3)-Cd(1)	95.15
C(18)-S(2)-Cd(1)	99.09	C(20)-S(2)-Cd(1)	102.39	C(22)-S(2)-Cd(1)	101.81
C(19)-S(3)-Cd(1)	100.58	C(21)-S(3)-Cd(1)	100.16	C(21)-S(1)-Cd(1)	98.18
C(17)- N(3)- Cd(1)	155.8	C(20)-N(4)-Cd(1)	140.7	C(21)-N(3)-Cd(1)	149.96
C(19)- N(4)- Cd(1)	144.3	C(19) -N(3)-Cd(1)	156.67	C(22)-N(4)-Cd(1)	141.04
C(18)- N(5)- Cd(1)	145.1	C(21) -N(5)-Cd(1)	147.99	C(23)-N(5)-Cd(1)	155.95
N(3)-C(17)-S(1)	179.4	N(4) -C(20)-S(2)	177.76	N(3) -C(21)-S(1)	179.09
N(5)-C(18)-S(2)	179.0	N(3) -C(19)-S(1)	179.40	N(4) -C(22)-S(2)	178.39
N(4)-C(19)-S(3)	178.8	N(5) -C(21)-S(3)	179.59	N(5) -C(23)-S(3)	179.08

Crystal Structures for dye1, 2 and 3

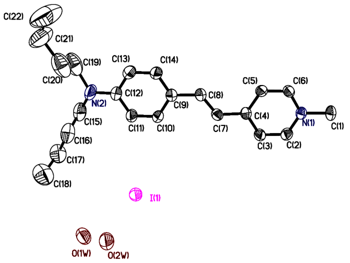
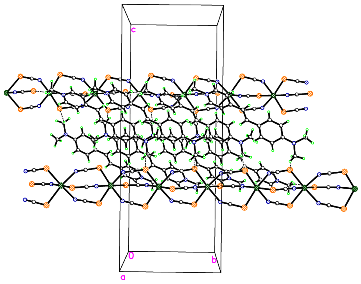


Fig. S1 ORTEP drawing of **1** with 50% probability ellipsoids.Hydrogen atoms have been omitted for clarity



Packing diagram of **1**

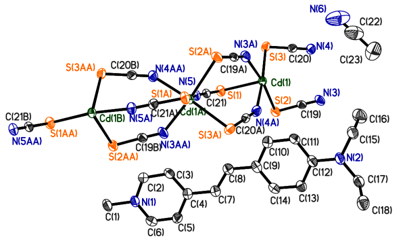
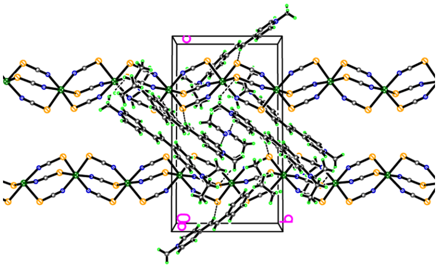


Fig. S2 ORTEP drawing of **2** with 50% probability ellipsoids.Hydrogen atoms have been omitted for clarity



Packing diagram of **2**

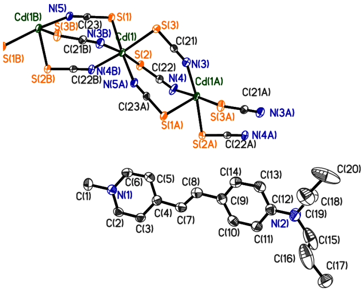
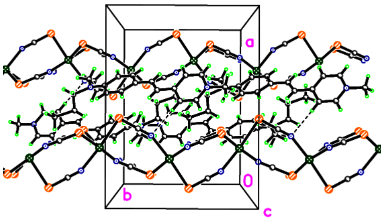


Fig. S3 ORTEP drawing of **3** with 50% probability ellipsoids.Hydrogen atoms have been omitted for clarity



Packing diagram of **3**

Two-photon fluorescence lifetime

From Table S5, we can see fluorescence lifetime of the dyes with the same anions slightly increases with the elongation of R chains. While the fluorescence lifetime of hybrid dyes is more longer than corresponding iodide analogues, which indicate that anions more or less participate in the process of two-photon absorption and emission. In addition, the influences of solvents on fluorescence lifetime have been studied as well. From experimental results, we got the following conclusions: (1) The fluorescence lifetime decreases with the increase of the solvent polarity. (1) P. Fromherz , J. Phys. Chem. 1995, **99**, 7188. 2) U. Narang, C. F. Zhao, J. D. Bhawalkar, F. V. Bright, and P. N. Prasad, J.

Chem. Phys., 1996, **100**, 4521. 3) Z. Q. Liu, Q. Fang, D, Wang, G. Xue, W. T. Yu, Z. S. Shao, M. H. Jiang, *Chemical Communications*, 2002, **23**, 2900.) (2) The viscosity constants of solvents may have very great influence on the two-photon absorption fluorescence lifetime. The big viscosity limits the rotation of the dye molecules, reducing conflictions among the dye molecules themselves and conflictions between the dye molecules and solvents molecules. All of these are in favor of two-photon fluorescence lifetime. (3) The planarity of the molecules will be destroyed by hydrogen bonds O–H···N between the H of hydroxyl group in methanol and the N from pyridinium ring in the dye molecules and the energy level structure of dye molecules will be changed as well, which decreases fluorescence lifetime. The fluorescence lifetimes of all dyes in methanol was rather short in the present work. The reason is that hydrogen bonds have played a role besides consideration of the influence of viscosity constants. In present work, the total charges of methylpyridinium are negative in excited state, which would further increase as the electrons transfer from D to A in the excited state, and this can make it rather easy to form strong hydrogen bonds between methanol molecules and the N atom from methylpyridine. Because of the strong hydrogen bond, equivalent to introducing methanol substituent group to N atom of pyridine ring, the planarity of the molecules will be destroyed, resulting in an easier transformation to non-radiation "TICT" state.

Table S5 Some photophysical properties and thermal properties

	Single-photon-related properties			Decomp.temp.
	Stokes (nm)	Φ^a	Two-photon Lifetime (ps)	TGA (°C)
1′	132	0.006	—	271
1	126	0.085	62	289
2′	119	0.009	67	281
2	116	0.034	75	290
3′	118	0.007	77	223
3	120	0.057	82	294
4′	119	0.008	87	274
4	115	0.039	71	294

[a] fluorescence quantum yield

Linear absorption spectra

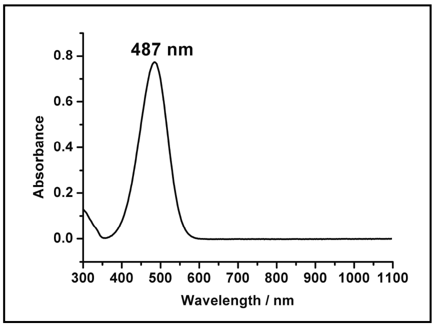


Fig. S4. UV-vis-near-IR absorption spectra of 4 in methanol with the concentration of 1.0 × 10^{-5} M.

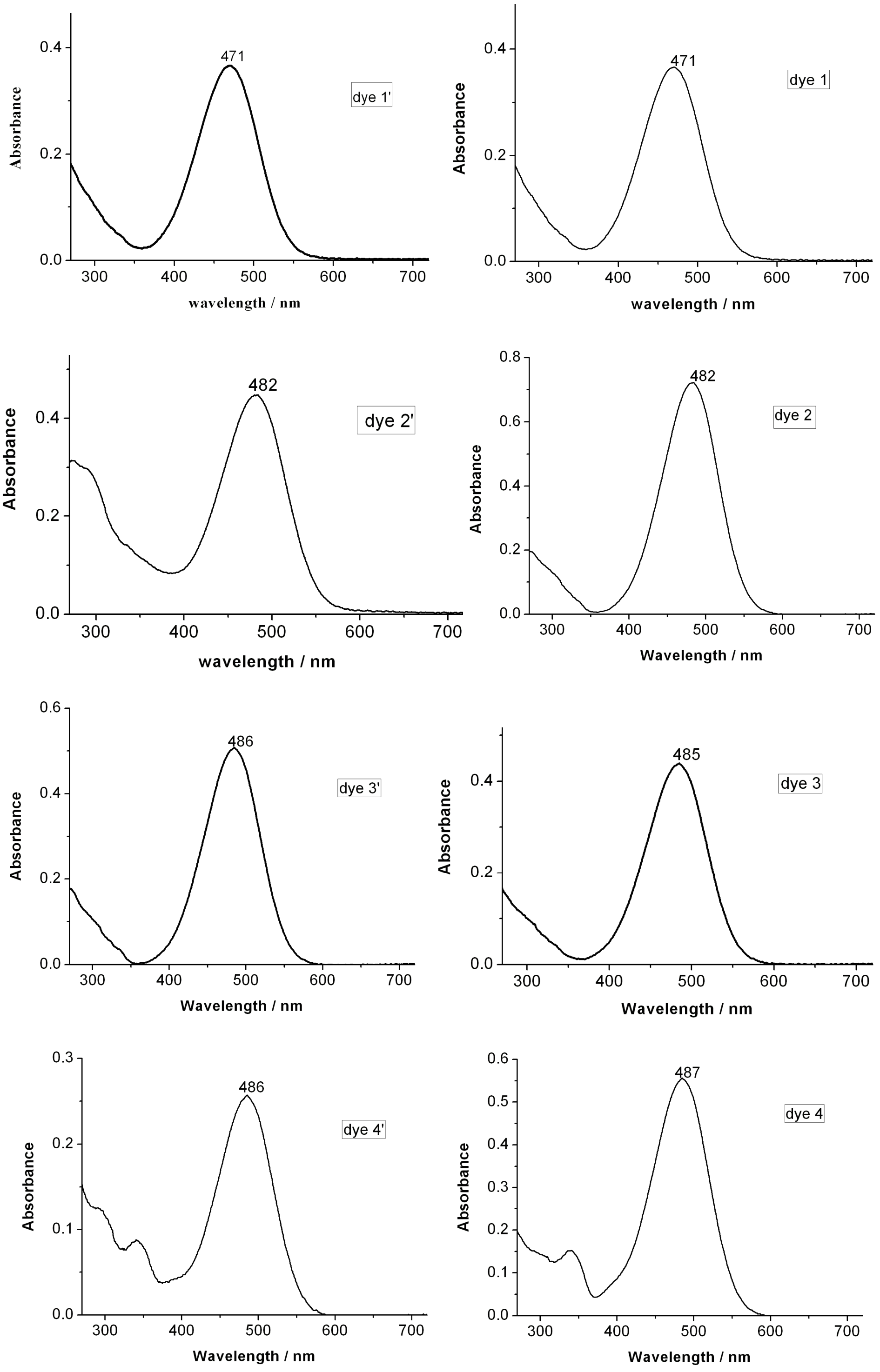


Fig. S5 UV absorption spectra of dye 1′-4′and dye 1-4 in methanol with the concentration of 1.0×10^{-5} M.

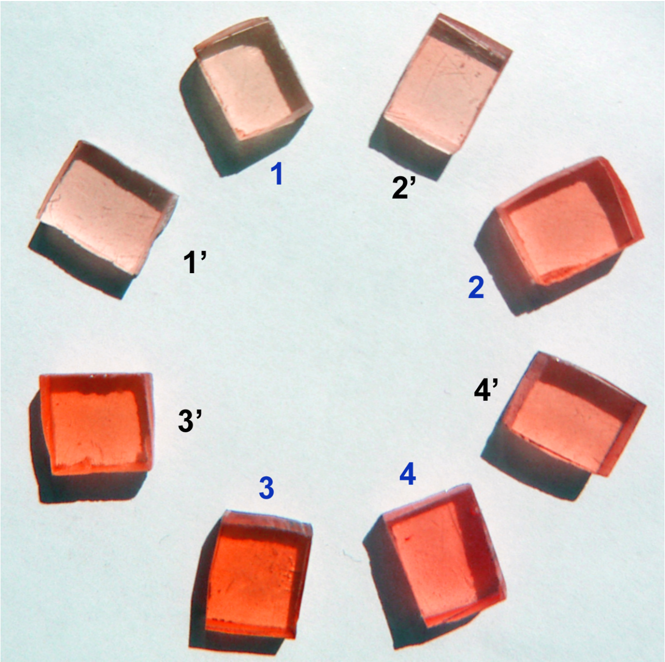


Fig. S6 Photograph of dye (0.2 - 0.4%) doped poly-methyl methacrylate