Supporting Information.

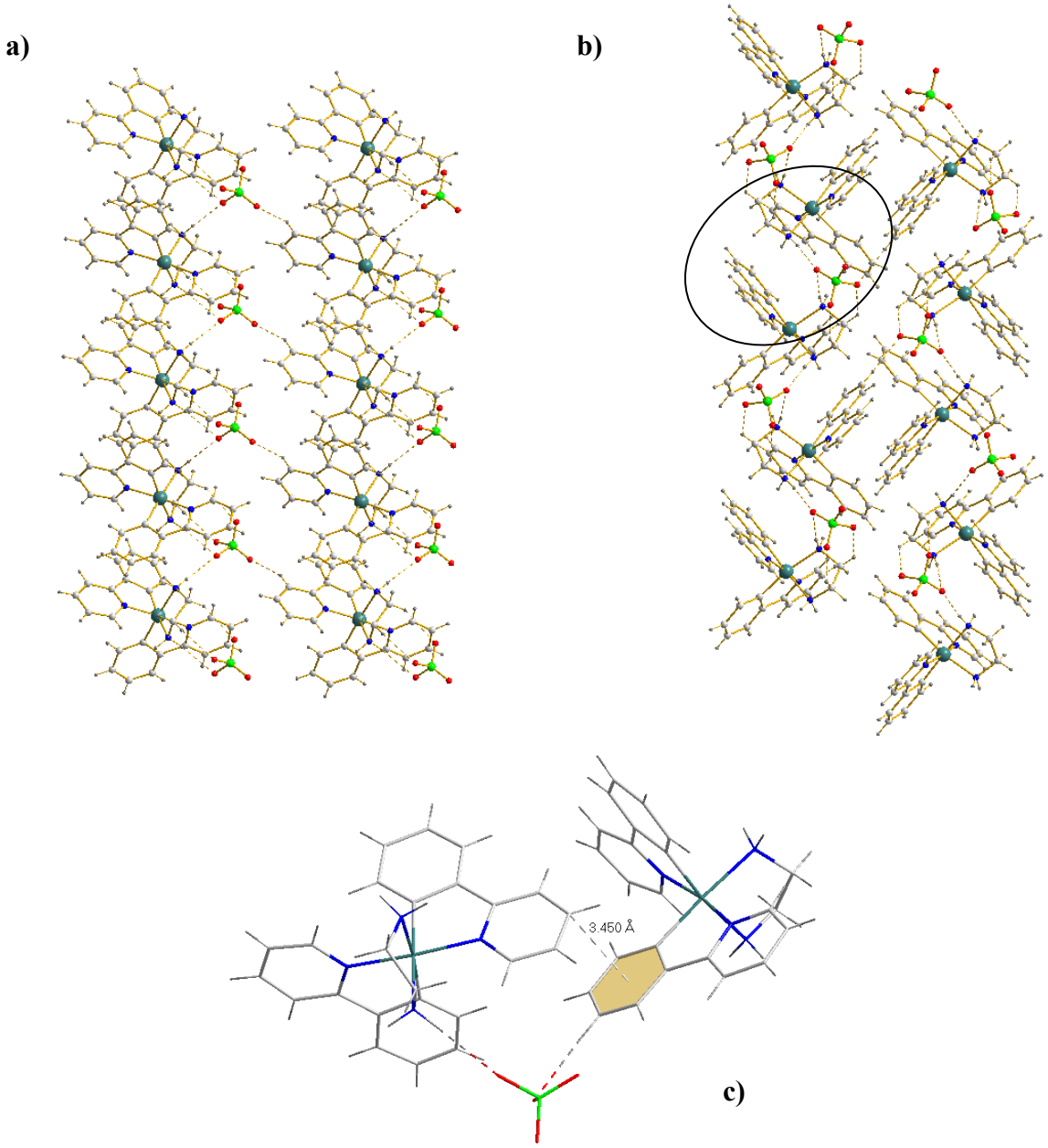

Figure S1. Side views of neighbouring supramolecular chains in **1c** along the *b* (a) and *c* (b) crystallographic directions. Details of the reciprocal arrangements of nearest phenylpyridine ligands, the dihedral angle between the mean planes being of 24.4° ca (c).

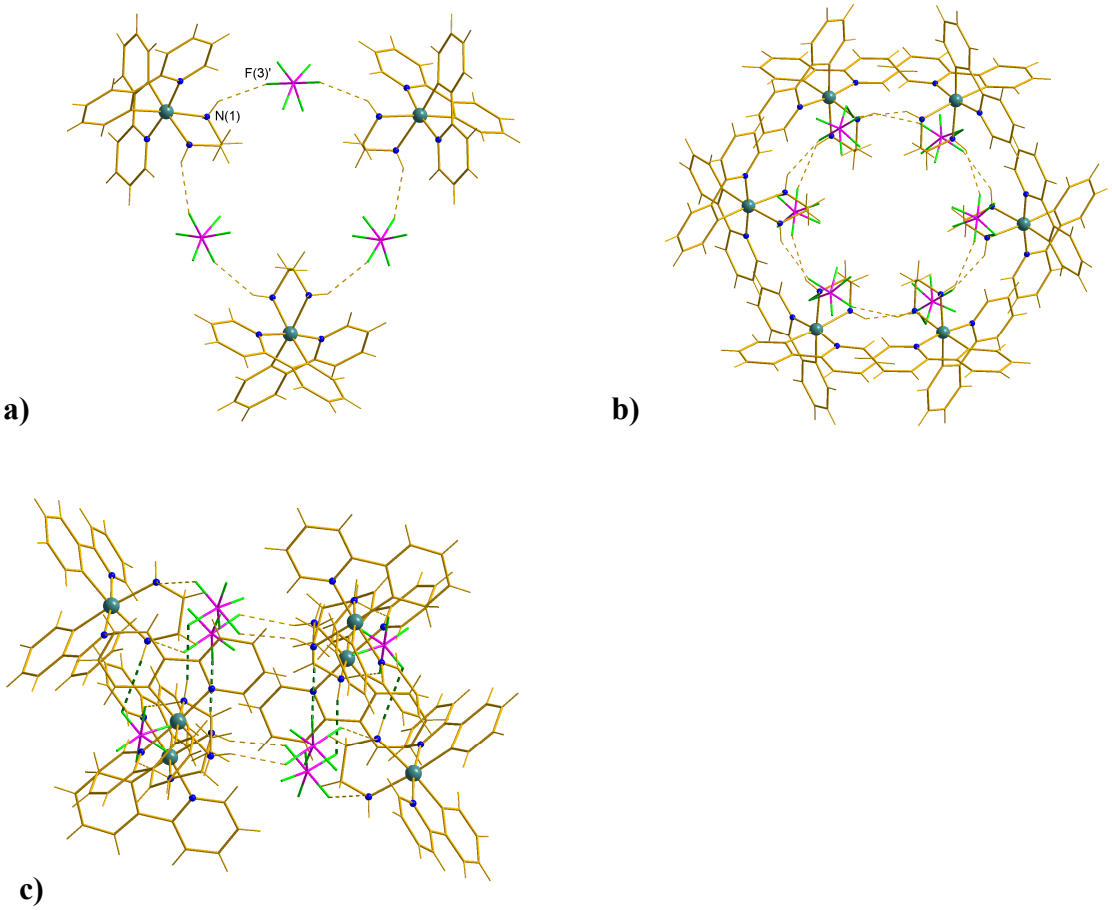

Figure S2. View of the supramolecular trinuclear units (a) in **2b**. Perspective (b) and side (c) view of the hexanuclear supramolecular motif assembled by means of intermolecular interactions between the trinuclear units in **2b**.

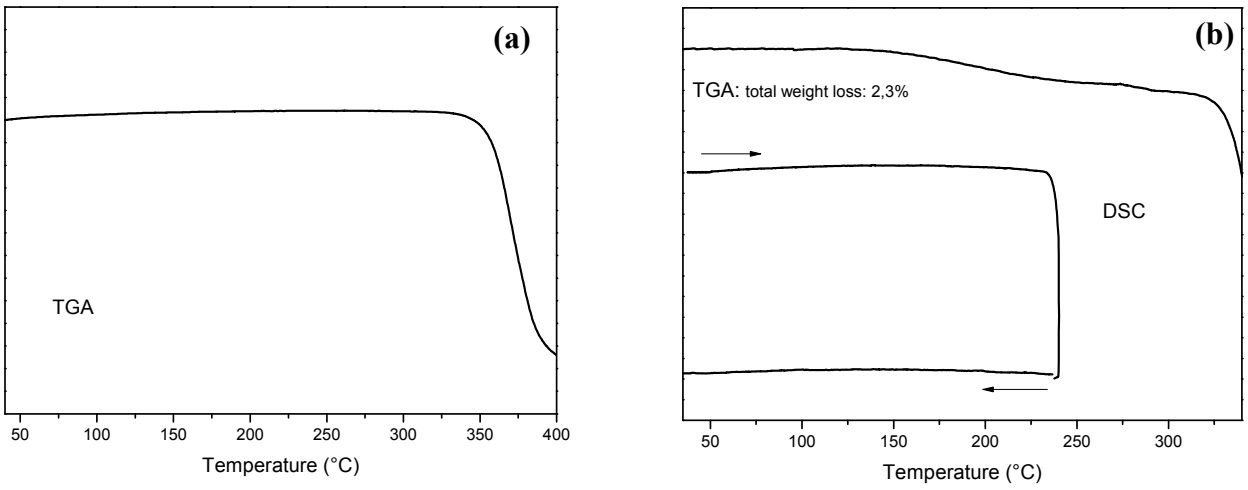

Figure S3. (a) TGA curve recoreded on crystalline sample of **2a**; **(b)** TGA and DSC curves recoreded on crystalline sample of **2b**

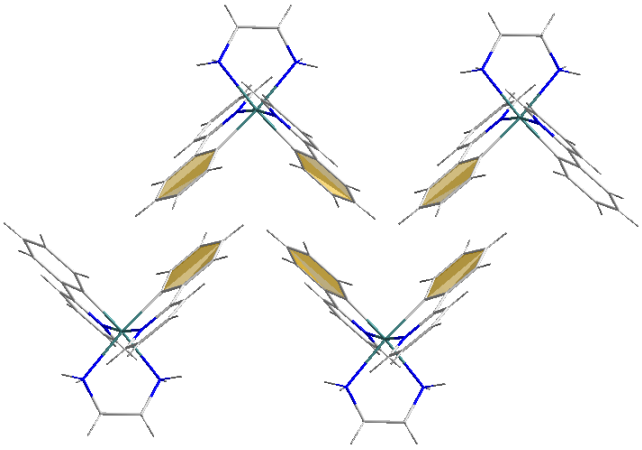

Figure S4. View of the π-π stacking interactions between the cyclometalated phenylpyridine ligands in **2b**.

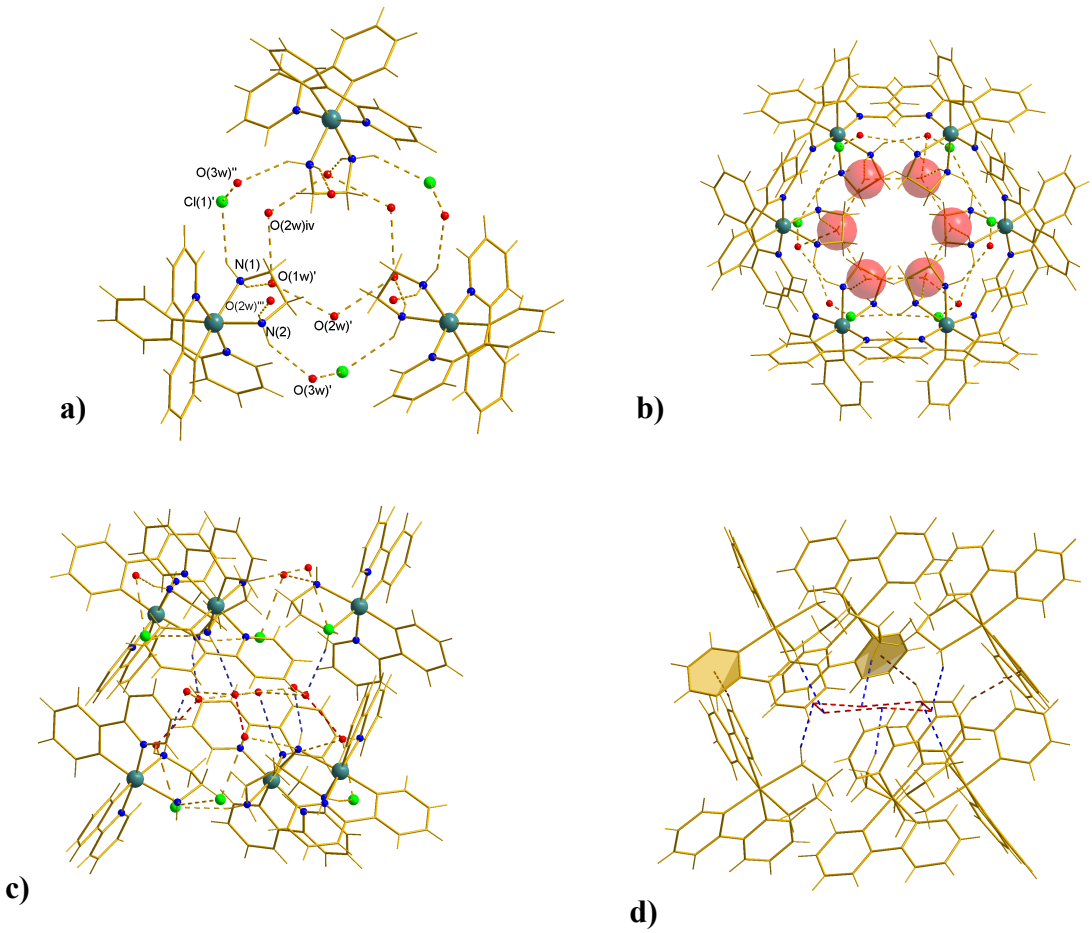

Figure S5. View of the supramolecular trinuclear unit supported by hydrogen bonding interactions in **3a** (a). Side (b) and perspective (c) view of the hexanuclear water cluster supported by hydrogen bonding interactions. View of the edge-to-face interactions involving phenylpyridine ligands of successive trinuclear supramolecular units (d).

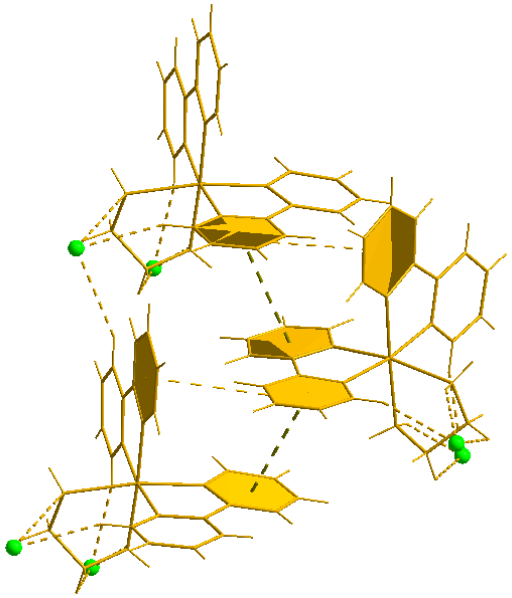

Figure S6. View of the π-π stacking and C-H···π edge-to-face interactions involving phenylpyridine ligands in **3b**.

Table S1. Crystal data and selected structure refinement parameters for 1c, 2a and 4a

Compound	1c	2a	4a
empirical formula	$C_{24}H_{24}ClIrN_4O_4$	$C_{24}H_{24}F_6IrN_4P$	$C_{48}H_{44}BIrN_4$
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	Pna2(1)	P-1	C2/c
Z	4	2	4
fw	660.12	705.64	879.88
a , Å	12.8971(17)	7.9909(6)	10.212(5)
b , Å	16.631(2)	10.6437(8)	26.279(11)
c , Å	10.9986(16)	14.8207(15)	14.334(6)
α, β, γ, deg	90, 90, 90	78.458(3), 81.685(4), 80.293(3)	90, 95.113(11), 90
V, $Å^3$	2359.2(6)	1209.32(18)	3831(3)
D_c, g cm-3	1.859	1.938	1.528
μ, □mm^{-1}	5.812	5.654	3.525
Independent reflections [R(int)]	7728 [0.0464]	4250 [0.0307]	4226 [0.0441]
Data/restraints/parameters	5447 / 1 / 326	3938 / 0 / 326	3885 / 0 / 245
Goodness-of-fit on F^2	0.894	1.101	1.080
Absolute structure parameter	-0.004(6)	-	-
[a]R1 [I > 2 σ (I)]	0.0256	0.0439	0.0236
[b,c]wR2	0.0509	0.1111	0.0588

$^a R1 = \sum ||F_o|-|F_c|| / \sum |F_o|$. $^b wR2 = \{ \sum [w(F_o^2-F_c^2)^2] / [(w(F_o^2)^2]\}^{1/2}$. $^c w = 1/[\sigma^2(F_o^2) + (aP)^2+bP]$ with $P = [F_o^2+2F_c^2]/3$, $a = 0.0278$ (**1c**), 0.0479 (**2a**), 0.0283 (**4a**), and $b = 0.00$ (**1c**), 8.98 (**2a**), 4.20 (**4a**).

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Table S2. Crystal data and selected structure refinement parameters for 2b, 3a and 3b

Compound	2b	3a	3b
empirical formula	$C_{26}H_{28}F_6IrN4O_{0.67}P$	$C_{24}H_{30}ClIrN_4O_3$	$C_{24}H_{24}ClIrN_4$2(CH_3OH) (H_20)
Crystal system	Trigonal	Trigonal	Monoclinic
Space group	P-3c1	R3c	Cc
Z	6	18	4
fw	744.36	650.17	678.22
a , Å	21.494(5)	29.092(7)	13.534(3)
b , Å	21.494(5)	29.092(7)	22.985(3)
c , Å	10.380(5)	15.193(4)	10.2524(14)
α, β, γ, deg	90, 90, 120	90, 90, 120	90,109.164(8),90
V, $Å^3$	4153(2)	11135(5)	3012.7(8)
D_c, g cm-3	1.786	1.745	1.495
μ, □mm^{-1}	4.946	5.536	4.551
Independent reflections [R(int)]	2971 [0.0576]	5450 [0.0389]	6634 [0.0408]
Data/restraints/parameters	2286 / 2 / 196	5291 / 1 / 298	6273 / 2 / 271
Goodness-of-fit on F^2	1.014	1.203	1.078
Absolute structure parameter	-	-0.004(7)	-0.004(5)
[a]R1 [I > 2 σ (I)]	0.0321	0.0174	0.0182
[b,c]wR2	0.0594	0.0443	0.0470

$^a R1 = \sum ||F_o|-|F_c|| / \sum |F_o|$. $^b wR2 = \{ \sum [w(F_o^2-F_c^2)^2] / [(w(F_o^2)^2]\}^{1/2}$. $^c w = 1/[\sigma^2(F_o^2) + (aP)^2+bP]$ with $P = [F_o^2+2F_c^2]/3$, $a =$ 0.0283 (**2b**), 0.0316(**3a**), 0.0270 (**3b**), and $b = 0.96$ (**2b**), 4.28 (**3a**), 0.00 (**3b**).

Table S3. Selected Bond lengths [Å] and angles [°] for compounds 1c-4a.

Compound	1c	2a	2b	3a	3b	4a
Ir(1)-C(1)	1.994(4)	2.009(8)	2.004(5)	1.990(6)	2.040(7)	2.003(3)
Ir(1)-C(12) [C(1a)]	2.008(4)	2.007(9)		2.009(6)	2.021(3)	
Ir(1)-N(3)	2.039(3)	2.042(7)	2.057(3)	2.043(4)	2.078(3)	2.050(3)
Ir(1)-N(4) [N3a]	2.057(3)	2.055(7)		2.054(5)	2.069(3)	
Ir(1)-N(1)	2.192(3)	2.207(7)	2.209(4)	2.203(5)	2.222(3)	2.180(3)
Ir(1)-N(2) [N(1a)]	2.198(3)	2.197(7)		2.204(5)	2.195(5)	
C(1)-Ir(1)-C(12)	91.4(2)	91.9(3)	90.2(2)	91.1 (2)	90.3(2)	93.4(2)
C(1)-Ir(1)-N(3)	81.0(2)	80.7(3)	80.5(2)	80.2(2)	80.9(2)	80.2(1)
C(12)-Ir(1)-N(3)	91.2(2)	94.5(3)		94.4(2)	96.1(1)	
C(1)-Ir(1)-N(4)	94.3(1)	94.5(3)	93.9 (2)	95.2(2)	90.9(2)	95.0(1)
C(12)-Ir(1)-N(4)	80.6(2)	80.5(3)		80.3(2)	79.9(1)	
N(3)-Ir(1)-N(4)	170.5(1)	173.0(3)	172.1(2)	173.0(2)	170.8(1)	173.1(1)
C(1)-Ir(1)-N(1)	92.2(1)	93.8(3)	174.3(2)	96.7(2)	98.5(1)	93.3(1)
C(12)-Ir(1)-N(1)	176.1(2)	174.2(3)		172.0(2)	171.1(1)	
N(3)-Ir(1)-N(1)	90.8(1)	86.4(3)	98.8(1)	88.6(2)	86.8(1)	86.9(1)
N(4)-Ir(1)-N(1)	97.6(1)	99.1(3)		97.3(2)	98.5(1)	
C(1)-Ir(1)-N(2)	170.6(1)	173.3(3)	95.5(2)	174.7(2)	177.7(2)	173.3(1)
C(12)-Ir(1)-N(2)	97.4(1)	94.8(3)		94.2(2)	92.4(1)	
N(3)-Ir(1)-N(2)	95.7(1)	99.0(3)	87.3(1)	99.1(2)	99.4(2)	98.4(1)
N(4)-Ir(1)-N(2)	90.1(1)	86.3(3)		86.0(2)	89.0(2)	
N(1)-Ir(1)-N(2)	79.1(1)	79.5(3)	78.8(2)	78.0(2)	78.7(1)	80.1(1)

Symmetry transformations used to generate equivalent atoms:

a) x-y+1,-y+2,-z+1/2 (**2b**) and -x+1,y,-z+3/2 (**4a**)

Table S4. Emission properties in solution

Emission at room temperature

	λ max (nm)[a]	λ max (nm)[b]	ϕ [a]	τ [a] (ns)	ϕ [b]	10^5x k_r [a] (s^{-1})	10^5x k_{nr} [a] (s^{-1})
1	498 (523)	502 (526)	0.68	1600	0.014	4.25	2
2	498 (523)	502 (526)	0.68	1600	0.015	4.25	2
3	498 (523)	502 (526)	0.68	1590	0.015	4.25	2
4	498 (523)	502 (526)	0.68	1570	0.015	4.25	2

[a]data for complexes **1-4** in degassed acetone; [b] data for complex in air equilibrated acetone.

Table S5. Luminescence lifetimes in solid crystalline organizations

Solid state luminescence lifetimes

	τ (ns) / Rel. Ampl.			
	λ_{max} 525 nm	λ_{max} 575 nm	λ_{max} 630 nm	λ_{max} 700 nm
1c	83 (12%) 250(59%) 590(29%)	119 (23%) 366 (58%) 1240(19%)	146 (15%) 507 (52 %) 1570(33%)	419 (28%) 920 (53 %) 2700(19%)
2a	353(41%) 795(59%)	394 (48 %) 941(52 %)	706 (65 %) 1830(35%)	813 (78 %) 2700(22%)
2b	3 (61 %) 6 (34 %) 48 (5 %)	3 (56 %) 30 (11 %) 300 (33 %)	6 (21%) 86 (22 %) 533 (57 %)	55 (18 %) 90 (3 %) 246 (40 %) 930 (39 %)
3a	23 (23 %) 58 (67 %) 225(10%)	23 (26 %) 64 (52 %) 428 (22 %)	32 (29 %) 120 (34%) 735 (37 %)	39 (16%) 155 (39 %) 820 (45%)
3b	4 (6%) 29 (42 %) 90 (52 %)	27 (13%) 96 (55 %) 390 (32%)	37 (17%) 150 (36 %) 710 (47 %)	56 (17 %) 230 (39 %) 880 (44 %)
4	19 (6%) 138(45%) 390(49%)	14 (3 %) 208 (44 %) 940 (53 %)	310 (22 %) 963 (58 %) 2500(20%)	370 (24 %) 965 (54 %) 2500(22%)